


ออกซีเดชันของแอลกอฮอล์โดยใช้เอนไซม์ไฮโดรอกซิเลส



นางสาวนวลักษณ์ ดุสิตสุวรรณ

สถาบันวิทยบริการ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

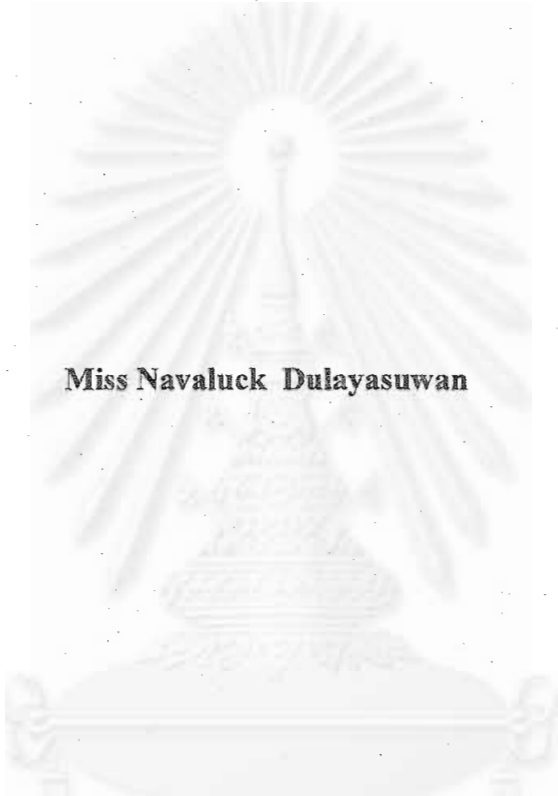
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2547

ISBN 974-17-5601-1

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

# **ALKENE OXIDATION USING SODIUM HYPOCHLORITE**



**Miss Navaluck Dulayasuwan**

**A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Petrochemistry and Polymer Science**

**Faculty of Science**

**Chulalongkorn University**

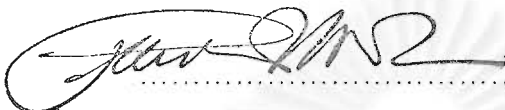
**Academic Year 2004**

**ISBN: 974-17-5601-1**

Thesis title                    ALKENE OXIDATION USING SODIUM HYPOCHLORITE  
By                                    Miss Navaluck Dulayasuwan  
Field of Study                Petrochemistry and Polymer Science  
Thesis Advisor               Associate Professor Amorn Petsom, Ph.D.


---


Accepted by the Faculty of Science, Chulalongkorn University in  
Partial Fulfillment of the Requirements for the Master's Degree


..... Dean of the Faculty of Science  
(Professor Piamsak Menasveta, Ph.D.)

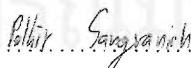
Thesis Committee

..... Chairman  
(Professor Pattarapan Prasassarakich, Ph.D.)

..... Thesis Advisor  
(Associate Professor Amorn Petsom, Ph.D.)

..... Member  
(Professor Sophon Roengsumran, Ph.D.)

..... Member  
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

..... Member  
(Assistant Professor Polkit Sangvanich, Ph.D.)

นวลักษณ์ ดุลยสุวรรณ: ออกซิเดชันของแอลคีนโดยใช้โซเดียมไฮโปคลอไรต์ (ALKENE OXIDATION USING SODIUM HYPOCHLORITE) อ.ที่ปรึกษา:  
รศ.ดร. อมร เพชรสม, 120 หน้า. ISBN: 974-17-5601-1

ปฏิกิริยาออกซิเดทีฟแฮโลเจเนชันของ 1-เฮกซีน 1, 5-เฮกซาไดอิน ไซโคลเฮกซีนและ เมทิลเมทาครีเลท โดยใช้โซเดียมไฮโปคลอไรต์ กรดแอซีติกและโซเดียมโบรไมด์เป็นตัวออกซิไดซ์ ในปฏิกิริยานี้ถ้าปราศจากโซเดียมโบรไมด์จะได้สารประกอบไดคลอไรด์เป็นผลผลิต ถ้าเติมโซเดียมโบรไมด์มากเกินไป (ประมาณ 10 เท่า) จะได้สารประกอบไดโบรไมด์ เป็นผลผลิตเพียงชนิดเดียว อย่างไรก็ตามถ้าปริมาณโซเดียมโบรไมด์อยู่ระหว่าง 1-5 เท่าจะให้ผลผลิตเป็นของผสมของสารประกอบไดแฮโลเจน เมื่อเติมตัวทำละลายร่วมลงไปในปฏิกิริยา เช่น ไอโซออกเทน และ เฮกเซน ไม่มีผลกับปริมาณผลผลิตที่เกิดขึ้น ซึ่งมีหลักฐานจากนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี และแมสสเปกโทรสโกปี กลไกของปฏิกิริยาเสนอว่าเกี่ยวข้องกับสารชั้นกลางแฮโลเนียมไอออน

สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.....

ลายมือชื่อนิติ นวลักษณ์ ดุลยสุวรรณ.....

ปีการศึกษา 2547.....

ลายมือชื่ออาจารย์ที่ปรึกษา.....

#4472298023: PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORD: OXIDATION/ ALKENE/ SODIUM HYPOCHLORITE/ OXIDATIVE HALOGENATION

NAVALUCK DULAYASUWAN: ALKENE OXIDATION USING SODIUM HYPOCHLORITE. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D. 120 pp. ISBN: 974-17-5601-1

Oxidative halogenation of 1-hexene, 1, 5-hexadiene, cyclohexene and methylmethacrylate using sodium hypochlorite, acetic acid and sodium bromide combination were carried out. Without bromide, dichlorocompounds were obtained. In the presence of excess bromide (10-fold excess), dibromocompounds were obtained exclusively. However, the amount of bromide between 1-5 fold excess gave a mixture of dihalocompounds. Co-solvents such as hexane and isooctane did not improve yield of the products. Moreover, the presence of co-solvent gave a mixture of products including haloalcohol as evidence by NMR spectroscopy and MS spectroscopy. The mechanism of this reaction was proposed to involve halonium ions intermediate.

จุฬาลงกรณ์มหาวิทยาลัย

Field of study Petrochemistry and polymer science Student's signature Navaluck Dulayasuman

Academic year 2004 Advisor's signature Amorn Petsom

## ACKNOWLEDGEMENTS

I would like to express my sincerest gratitude to my advisor, Associate Professor Dr. Amorn Petsom. Without his instruction, suggestion, assistance and encouragement this research would not have been accomplished.

I am very appreciative to the chairman and members of thesis committee, Professor Dr. Pattarapan Prasassarakich, Professor Dr. Sophon Roengsumran, Assistant Professor Dr. Warinthorn Chavasiri and Assistant Professor Dr. Polkit Sangvanich for their valuable comments and helping me to improve the quality of my thesis.

I am also very much appreciate to the Chemistry Department, Chulalongkorn University for IR and NMR facilities. Partial financial support from the Graduate School is gratefully acknowledged.

Finally, I would like to express my appreciation to my family for their kindness, encouragement and supports throughout the course of my education and my friends for their friendship, encouragement and assistance during my research. Without them, I would have never been able to achieve this goal.

จุฬาลงกรณ์มหาวิทยาลัย

# CONTENTS

	PAGE
ABSTRACT (IN THAI).....	iv
ABSTRACT (IN ENGLISH).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	ix
LIST OF FIGURES.....	x
LIST OF ABBREVIATIONS.....	xv
CHAPTER.....	1
<b>I INTRODUCTION</b> .....	1
1.1 Introduction.....	1
1.2 Objectives and scope of the research.....	2
<b>II THEORY AND LITERATURE REVIEW</b> .....	4
2.1 Addition to multiple carbon-carbon bonds.....	4
2.2 Stepwise electrophilic addition to $H_2C=CH_2$ .....	4
2.3 Kinetics of electrophilic addition reactions.....	5
2.4 Direction and stereochemistry addition reactions.....	7
2.5 Oxidation Reaction.....	8
2.6 Sodium hypochlorite.....	10
2.8 Literatures review.....	10
<b>III EXPERIMENTAL</b> .....	15
3.1 General methods.....	15
3.2 Chemicals.....	15
3.3 Experimental procedure.....	15
3.3.1. Oxidative halogenation of 1-hexene.....	15





## LIST OF TABLES

	PAGE
<b>Table 2.1</b> Relative rate of different alkenes.....	6
<b>Table 4.1</b> Oxidative hlogenation of 1-hexene.....	35
<b>Table 4.2</b> Simple normalization-integrator of GC-MS in the group of 1-hexene derivatives.....	36
<b>Table 4.3</b> Comparison of oxidative bromination of 1-hexene using NaOCl and KBr/ CAN.....	37
<b>Table 4.4</b> Oxidative halogenation of cyclohexene derivatives.....	38
<b>Table 4.5</b> Simple normalization-integrator of GC-MS in the group of cyclohexene derivatives.....	39
<b>Table 4.6</b> Comparison of oxidative bromination of 1-hexene using NaOCl and others method.....	39
<b>Table 4.7</b> Oxidative halogenation of MMA derivatives.....	40
<b>Table 4.8</b> Simple normalization-integrator of GC-MS in the group of MMA derivatives.....	41
<b>Table 4.9</b> Oxidative halogenation of 1, 5-hexadiene.....	41
<b>Table 4.10</b> Simple normalization-integrator of GC-MS in the group of 1, 5-hexadiene derivatives.....	42
<b>Table 4.11</b> Comparison of oxidative bromination of 1-hexene using NaOCl and other method.....	43
<b>Table 4.12</b> The % composition of 1-hexene derivatives.....	44

สถาบันวิทยบริการ  
 จุฬาลงกรณ์มหาวิทยาลัย

## LIST OF FIGURES

	PAGE
<b>Figure4.1</b> The structures of 1-hexene derivatives.....	35
<b>Figure4.2</b> Mechanism of halogenation.....	36
<b>Figure4.3</b> The structures of cyclohexene derivatives.....	38
<b>Figure4.4</b> The structures of MMA derivatives.....	40
<b>Figure4.5</b> The structures of 1, 5-hexadiene derivatives.....	42
<b>Figure4.6</b> Mechanism of tetrabromoalkane.....	43
<b>FigureA1</b> The FTIR spectrum of mixture 1H.....	51
<b>FigureA2</b> The <sup>1</sup> H-NMR spectrum of mixture 1H.....	51
<b>FigureA3</b> The <sup>13</sup> C-NMR spectrum of mixture 1H.....	52
<b>FigureA4</b> The gas chromatogram of mixture 1H.....	52
<b>FigureA5</b> The mass spectrum of mixture 1H at t <sub>R</sub> = 8.04 min .....	53
<b>FigureA6</b> The mass spectrum of mixture 1H at t <sub>R</sub> = 10.58 min .....	53
<b>FigureA7</b> The mass spectrum of mixture 1H at t <sub>R</sub> = 16.62 min .....	54
<b>FigureA8</b> The FTIR spectrum of mixture 2H.....	54
<b>FigureA9</b> The <sup>1</sup> H-NMR spectrum of mixture 2H.....	55
<b>FigureA10</b> The <sup>13</sup> C-NMR spectrum of mixture 2H.....	55
<b>FigureA11</b> The gas chromatogram of mixture 2H.....	56
<b>FigureA12</b> The mass spectrum of mixture 2H at t <sub>R</sub> = 10.73 min .....	56
<b>FigureA13</b> The FTIR spectrum of mixture 3H.....	57
<b>FigureA14</b> The <sup>1</sup> H-NMR spectrum of mixture 3H.....	57
<b>FigureA15</b> The <sup>13</sup> C-NMR spectrum of mixture 3H.....	58
<b>FigureA16</b> The gas chromatogram of mixture 3H.....	58
<b>FigureA17</b> The mass spectrum of mixture 3H at t <sub>R</sub> = 10.72 min .....	59
<b>FigureA18</b> The FTIR spectrum of mixture 4H.....	59
<b>FigureA19</b> The <sup>1</sup> H-NMR spectrum of mixture 4H.....	60
<b>FigureA20</b> The <sup>13</sup> C-NMR spectrum of mixture 4H.....	60
<b>FigureA21</b> The gas chromatogram of mixture 4H.....	61
<b>FigureA22</b> The mass spectrum of mixture 4H at t <sub>R</sub> = 10.72 min .....	61
<b>FigureA23</b> The FTIR spectrum of mixture 5H.....	62

## LIST OF FIGURES (CONTINUED)

	PAGE
<b>FigureA24</b> The $^1\text{H}$ -NMR spectrum of mixture 5H.....	62
<b>FigureA25</b> The $^{13}\text{C}$ -NMR spectrum of mixture 5H.....	63
<b>FigureA26</b> The gas chromatogram of mixture 5H.....	63
<b>FigureA27</b> The mass spectrum of mixture 5H at $t_{\text{R}}= 10.59$ min .....	64
<b>FigureA28</b> The mass spectrum of mixture 5H at $t_{\text{R}}= 16.61$ min .....	64
<b>FigureA29</b> The FTIR spectrum of mixture 6H.....	65
<b>FigureA30</b> The $^1\text{H}$ -NMR spectrum of mixture 6H.....	65
<b>FigureA31</b> The $^{13}\text{C}$ -NMR spectrum of mixture 6H.....	66
<b>FigureA32</b> The gas chromatogram of mixture 6H.....	66
<b>FigureA33</b> The mass spectrum of mixture 6H at $t_{\text{R}}= 10.72$ min .....	67
<b>FigureA34</b> The mass spectrum of mixture 6H at $t_{\text{R}}= 16.30$ min .....	67
<b>FigureA35</b> The FTIR spectrum of mixture 7H.....	68
<b>FigureA36</b> The $^1\text{H}$ -NMR spectrum of mixture 7H.....	68
<b>FigureA37</b> The $^{13}\text{C}$ -NMR spectrum of mixture 7H.....	69
<b>FigureA38</b> The gas chromatogram of mixture 7H.....	69
<b>FigureA39</b> The mass spectrum of mixture 7H at $t_{\text{R}}= 10.73$ min .....	70
<b>FigureA40</b> The mass spectrum of mixture 7H at $t_{\text{R}}= 16.30$ min .....	70
<b>FigureA41</b> The FTIR spectrum of mixture 8H.....	71
<b>FigureA42</b> The $^1\text{H}$ -NMR spectrum of mixture 8H.....	71
<b>FigureA43</b> The $^{13}\text{C}$ -NMR spectrum of mixture 8H.....	72
<b>FigureA44</b> The gas chromatogram of mixture 8H.....	72
<b>FigureA45</b> The mass spectrum of mixture 8H at $t_{\text{R}}= 8.03$ min .....	73
<b>FigureA46</b> The mass spectrum of mixture 8H at $t_{\text{R}}= 10.57$ min .....	73
<b>FigureA47</b> The mass spectrum of mixture 8H at $t_{\text{R}}= 16.60$ min .....	74
<b>FigureA48</b> The FTIR spectrum of mixture 9H.....	74
<b>FigureA49</b> The $^1\text{H}$ -NMR spectrum of mixture 9H.....	75
<b>FigureA50</b> The $^{13}\text{C}$ -NMR spectrum of mixture 9H.....	75
<b>FigureA51</b> The gas chromatogram of mixture 9H.....	76
<b>FigureA52</b> The mass spectrum of mixture 9H at $t_{\text{R}}= 10.74$ min .....	76
<b>FigureA53</b> The FTIR spectrum of mixture 10H.....	77

## LIST OF FIGURES (CONTINUED)

	PAGE
<b>FigureA54</b> The $^1\text{H}$ -NMR spectrum of mixture 10H.....	77
<b>FigureA55</b> The $^{13}\text{C}$ -NMR spectrum of mixture 10H.....	78
<b>FigureA56</b> The gas chromatogram of mixture 10H.....	78
<b>FigureA57</b> The mass spectrum of mixture 10H at $t_{\text{R}}= 10.74$ min .....	79
<b>FigureB1</b> The FTIR spectrum of mixture 1C.....	81
<b>FigureB2</b> The $^1\text{H}$ -NMR spectrum of mixture 1C.....	81
<b>FigureB3</b> The $^{13}\text{C}$ -NMR spectrum of mixture 1C.....	82
<b>FigureB4</b> The gas chromatogram of mixture 1C.....	82
<b>FigureB5</b> The mass spectrum of mixture 1C at $t_{\text{R}}= 9.33$ min .....	83
<b>FigureB6</b> The mass spectrum of mixture 1C at $t_{\text{R}}= 11.82$ min .....	83
<b>FigureB7</b> The mass spectrum of mixture 1C at $t_{\text{R}}= 18.77$ min .....	84
<b>FigureB8</b> The FTIR spectrum of mixture 2C.....	84
<b>FigureB9</b> The $^1\text{H}$ -NMR spectrum of mixture 2C.....	85
<b>FigureB10</b> The $^{13}\text{C}$ -NMR spectrum of mixture 2C.....	85
<b>FigureB11</b> The gas chromatogram of mixture 2C.....	86
<b>FigureB12</b> The mass spectrum of mixture 2C at $t_{\text{R}}= 10.75$ min .....	86
<b>FigureB13</b> The mass spectrum of mixture 2C at $t_{\text{R}}= 12.11$ min .....	87
<b>FigureB14</b> The mass spectrum of mixture 2C at $t_{\text{R}}= 21.01$ min .....	87
<b>FigureB15</b> The FTIR spectrum of mixture 3C.....	88
<b>FigureB16</b> The $^1\text{H}$ -NMR spectrum of mixture 3C.....	88
<b>FigureB17</b> The $^{13}\text{C}$ -NMR spectrum of mixture 3C.....	89
<b>FigureB18</b> The gas chromatogram of mixture 3C.....	89
<b>FigureB19</b> The mass spectrum of mixture 3C at $t_{\text{R}}= 10.73$ min .....	90
<b>FigureB20</b> The mass spectrum of mixture 3C at $t_{\text{R}}= 12.12$ min .....	90
<b>FigureB21</b> The mass spectrum of mixture 3C at $t_{\text{R}}= 12.96$ min .....	91
<b>FigureB22</b> The FTIR spectrum of mixture 4C.....	91
<b>FigureB23</b> The $^1\text{H}$ -NMR spectrum of mixture 4C.....	92
<b>FigureB24</b> The $^{13}\text{C}$ -NMR spectrum of mixture 4C.....	92
<b>FigureC1</b> The FTIR spectrum of mixture 1M.....	94
<b>FigureC2</b> The $^1\text{H}$ -NMR spectrum of mixture 1M.....	94

## LIST OF FIGURES (CONTINUED)

	PAGE
<b>FigureC3</b> The $^{13}\text{C}$ -NMR spectrum of mixture 1M.....	95
<b>FigureC4</b> The gas chromatogram of mixture 1M.....	95
<b>FigureC5</b> The mass spectrum of mixture 1M at $t_{\text{R}}= 10.19$ min .....	96
<b>FigureC6</b> The mass spectrum of mixture 1M at $t_{\text{R}}= 16.65$ min .....	96
<b>FigureC7</b> The FTIR spectrum of mixture 2M.....	97
<b>FigureC8</b> The $^1\text{H}$ -NMR spectrum of mixture 2M.....	97
<b>FigureC9</b> The $^{13}\text{C}$ -NMR spectrum of mixture 2M.....	98
<b>FigureC10</b> The gas chromatogram of mixture 2M.....	98
<b>FigureC11</b> The mass spectrum of mixture 2M at $t_{\text{R}}= 10.51$ min .....	99
<b>FigureC12</b> The FTIR spectrum of mixture 3M.....	99
<b>FigureC13</b> The $^1\text{H}$ -NMR spectrum of mixture 3M.....	100
<b>FigureC14</b> The $^{13}\text{C}$ -NMR spectrum of mixture 3M.....	100
<b>FigureC15</b> The gas chromatogram of mixture 3M.....	101
<b>FigureC16</b> The mass spectrum of mixture 3M at $t_{\text{R}}= 10.48$ min .....	101
<b>FigureC17</b> The FTIR spectrum of mixture 4M.....	102
<b>FigureC18</b> The $^1\text{H}$ -NMR spectrum of mixture 4M.....	102
<b>FigureC19</b> The $^{13}\text{C}$ -NMR spectrum of mixture 4M.....	103
<b>FigureC20</b> The gas chromatogram of mixture 4M.....	103
<b>FigureC21</b> The mass spectrum of mixture 4M at $t_{\text{R}}= 10.49$ min .....	104
<b>FigureD1</b> The FTIR spectrum of mixture 1HD.....	106
<b>FigureD2</b> The $^1\text{H}$ -NMR spectrum of mixture 1HD.....	106
<b>FigureD3</b> The $^{13}\text{C}$ -NMR spectrum of mixture 1HD.....	107
<b>FigureD4</b> The gas chromatogram of mixture 1HD.....	107
<b>FigureD5</b> The mass spectrum of mixture 1HD at $t_{\text{R}}= 14.62$ min .....	108
<b>FigureD6</b> The mass spectrum of mixture 1HD at $t_{\text{R}}= 16.10$ min .....	108
<b>FigureD7</b> The mass spectrum of mixture 1HD at $t_{\text{R}}= 16.17$ min .....	109
<b>FigureD8</b> The FTIR spectrum of mixture 2HD.....	109
<b>FigureD9</b> The $^1\text{H}$ -NMR spectrum of mixture 2HD.....	110
<b>FigureD10</b> The $^{13}\text{C}$ -NMR spectrum of mixture 2HD.....	110
<b>FigureD11</b> The gas chromatogram of mixture 2HD.....	111

## LIST OF FIGURES (CONTINUED)

	PAGE
<b>FigureD12</b> The mass spectrum of mixture 2HD at $t_R= 17.84$ min .....	111
<b>FigureD13</b> The mass spectrum of mixture 2HD at $t_R= 17.90$ min .....	112
<b>FigureD14</b> The mass spectrum of mixture 2HD at $t_R= 18.91$ min .....	112
<b>FigureD15</b> The FTIR spectrum of mixture 3HD.....	113
<b>FigureD16</b> The $^1\text{H-NMR}$ spectrum of mixture 3HD.....	113
<b>FigureD17</b> The $^{13}\text{C-NMR}$ spectrum of mixture 3HD.....	114
<b>FigureD18</b> The gas chromatogram of mixture 3HD.....	114
<b>FigureD19</b> The mass spectrum of mixture 3HD at $t_R= 17.84$ min .....	115
<b>FigureD20</b> The mass spectrum of mixture 3HD at $t_R= 17.90$ min .....	115
<b>FigureD21</b> The mass spectrum of mixture 3HD at $t_R= 18.93$ min .....	116
<b>FigureD22</b> The FTIR spectrum of mixture 4HD.....	116
<b>FigureD23</b> The $^1\text{H-NMR}$ spectrum of mixture 4HD.....	117
<b>FigureD24</b> The $^{13}\text{C-NMR}$ spectrum of mixture 4HD.....	117
<b>FigureD25</b> The gas chromatogram of mixture 4HD.....	118
<b>FigureD26</b> The mass spectrum of mixture 4HD at $t_R= 18.93$ min .....	118
<b>FigureD27</b> The mass spectrum of mixture 4HD at $t_R= 18.93$ min .....	119
<b>FigureD28</b> The mass spectrum of mixture 4HD at $t_R= 18.93$ min .....	119

## LIST OF ABBREVIATIONS

C	Cyclohexene
CAN	Cerium (IV) ammonium nitrate
$^{13}\text{C-NMR}$	Carbon-13 Nuclear Magnetic Resonance
$^{\circ}\text{C}$	Degree celsius
$\text{cm}^{-1}$	Unit of wavw number
d	Doublet (NMR)
FT-IR	Fourier Transform Infrared Spectroscopy
g	Gram (s)
H	1-hexene
HD	1, 5-hexadiene
$^1\text{H-NMR}$	Proton Nuclear Magnetic Resonance
MMA	methylmethacrylate
mmol	Millimole (s)
ml	Milliliter (s)
m	Multiplet (NMR)
ppm	Part per million
$R_f$	Retardation factor in chromatography
s	Singlet (NMR)
TLC	Thin layer chromatography
t	Triplet(NMR)
$t_R$	Retention Time
$\gamma$	Unit of interfacial tention
$\delta$	Unit of chemical shift

# CHAPTER I

## INTRODUCTION

### 1.1 Introduction

Halogenated organic compounds form an important class of intermediates. They can be converted efficiently into other functional groups by simple chemical transformations.

In general, halogenation reactions can be carried out using halogen compounds such as bromine ( $\text{Br}_2$ ), chlorine ( $\text{Cl}_2$ ) and iodine ( $\text{I}_2$ ) in carbon tetrachloride ( $\text{CCl}_4$ ) with/ without catalyst. However, these compounds are dangerous to handle in large scale applications.

The halogenation of alkenes are an important organic transformation and it is worthy to note that protection and deprotection of double bonds *via* halogenation-dehalogenation strategy is finding increasing more applications in organic synthesis. A number of protocols are available to achieve the halogenation of alkenes [1].

Recently, the oxidative bromination of cyclohexene and 1-hexene were carried out using cerium (IV) ammonium nitrate (CAN) and potassium bromide in dichloromethane and gave 65 % of 1,2-dibromocyclohexane and 82% of 1,2-dibromohexane, respectively [1].

A mild and efficient method for the bromination of activated aromatic compounds using LiBr as the bromine source and CAN as the oxidant has been reported [2].

Sodium bromate and potassium bromate are commercially available, they are very stable solid which can be handled much more easily than liquid bromine or hypobromous acid solution. Oxidation with bromates results in bromide ion formation, which can be safely treated or recycled. Bromate salt can oxidize primary alcohols to aldehydes, secondary alcohols to ketones and under different sets of conditions the oxidation can result in the formation of esters [3].

Oxidative bromination of methylantranilate using sodium perborate ( $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ) and potassium bromide is recommended as a cheap, safe and convenient alternative to  $\text{H}_2\text{O}_2/\text{NaBr}$  [4].



Sodium hypochlorite (NaOCl), a versatile and easily handling oxidizing agent, can be used in the oxidation of alkenes, alcohols, aldehydes, amines and thiol, thioether as well as a reagent for N-chlorination, oxidative coupling and degradation reactions [5]. Usually sodium hypochlorite is used as oxidizing agent for oxidation reaction with high yield of product, under mild condition, inexpensive and safe.

In spite of the variety of reagents available for oxidative halogenation, lack of selectivity and unwanted side reactions are the major problems. Recently, oxidative halogenation of aromatic compounds using sodium hypochlorite and sodium bromide in acetic acid is reported as a novel method [6].

This research work, therefore, would like to apply this novel method in the oxidative halogenation reaction of alkenes.

## **1.2 Objectives and scope of the research**

### **1.2.1 Objectives**

1. To study the new chemical process for alkene oxidative halogenation using sodium hypochlorite with/ without sodium bromide.
2. To investigate the effect of 1) solvents 2) ratio of substrate, sodium hypochlorite and sodium bromide on oxidative halogenation reaction.

### **1.2.2 Scopes of research**

1. Literature survey of relevant research works
2. Oxidative halogenation of:
  - a. 1-hexene
  - b. 1, 5-hexadiene
  - c. cyclohexene
  - d. methylmethacrylate

3. Investigation on the effects of the following parameters:
  - a. solvent
  - b. ratio of substrate and sodium hypochlorite
  - c. ratio of substrate and sodium bromide
4. Discussion and conclusion.



จุฬาลงกรณ์มหาวิทยาลัย

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Addition to multiple carbon-carbon bonds [7]

The characteristic reaction of alkenes are the addition of halogen, hydrogen halide, sulphuric acid, hypohalous acid, ozone, salts of heavy metals and other reagents, oxidation and polymerization reactions.

Basically, there are four ways in which addition to a double bond may take place. Three of these are two-step process, with the initial attack by an electrophile, nucleophile or a free radical to give an intermediate followed by a second step consisting of the combination of the resulting intermediate with a negative species, a positive species or a neutral entity. In the fourth type of mechanism, attack at the two sides of the double bond is simultaneous. Which of the four mechanism is operating in any given case is determined of by the nature of substrate, reagent, and reaction conditions. As the  $\pi$ -electron of the  $\pi$ -bond shield the molecule, the alkenes will not be expected to be attacked by a nucleophile, unless the doubly bond carbon atoms are linked to electron withdrawing groups because of the repulsive forces operating between the negatively charged  $\pi$ -electron cloud and the negative charge on a nucleophile. Therefore *the addition to carbon-carbon double bond are mostly electrophilic in nature.*

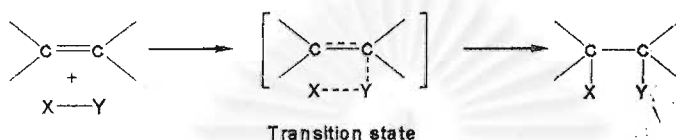
#### 2.2 Stepwise electrophilic addition to $\text{H}_2\text{C}=\text{CH}_2$

A particularly significant observation concerning the mechanism of electrophilic addition to double bond is that they proceed in the dark and in the presence of free radical absorbers and are accelerated that addition by the presence of small amounts of moisture. This suggests that addition to the double bond is proceeded by its polarization, the shifting of the  $\pi$ -electron pair towards one of the carbon atoms:



The mechanism of these addition reactions is therefore polar. When any molecular, X-Y, adds to a double bond, the reaction may take place in two ways :

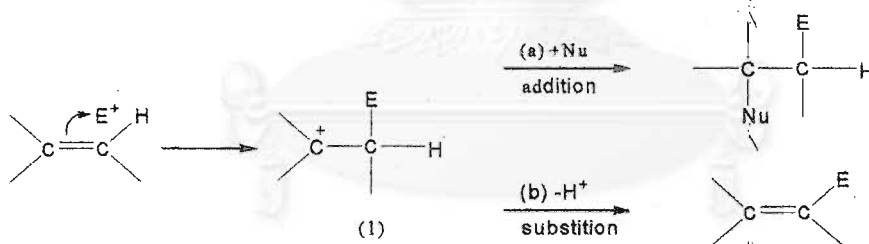
(i) Two parts of the molecule, X and Y, may add simultaneously through the formation of a four-centred transition state :



(ii) The addition of X-Y may be stepwise. The first step is the attack of the electrophilic part of the addendum (molecule being added) to give an intermediate carbonium ion (1), which has two courses to proceed :

- (a) Addition of the nucleophilic part of the addendum, or
- (b) Loss of a proton, leading to a substitution reaction.

The overall stepwise reaction can be represented as,



Most of the polar reaction do not seem to be simple four centred one-step processes [as (i)] for two important reasons. Firstly, both the new bonds on the same side of the double bond and hence produce a cis-adduct. However, there is ample evidence to show that the reagents add to give trans-addition products.

### 2.3 Kinetics of electrophilic addition reactions

The addition of molecules like  $X_2$ ,  $HX$  etc. to an unsaturated compound in usual solvents, like water, alcohol or aqueous acetic acid is generally a second order

reaction. In acetic acid, the addition of bromine takes place as a third order reaction. The effect of the structure of alkene on the rate of such a third order reaction is the same as on the second order reaction. Thus the third order bromination differs insignificantly in mechanism from the second-order reaction.

It has been confirmed by measuring the relative rates of addition of iodine and interhalogen compounds like iodine bromide, iodine chloride and bromine chloride in acetic acid solution (all of which are third order reactions), that in the first step of the reaction an electrophilic attacks the alkene. As only a few of the collisions between the electrophilic and the neutral molecule result in the formation of a halogen-carbon bond, this step is the slowest one and therefore is rate determining. As the rate of the overall addition reaction is dependent upon the rate of this first step, let us examine the factors governing the rate of this step.

Electrophilic attack on a double bond depends upon the avail ability of an electron pair in the  $\pi$ -orbital. If this  $\pi$ -electron density is somewhat diluted either through resonance or by inductive effect of a group linked to the alkene double bond, the rate of the addition reactions will be governed by the nature, the electron withdrawing or repelling properties of the  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  groups on the alkene  $R_1R_2C=CR_3R_4$ . This is illustrated by considering the rates of addition of bromine to different alkenes in  $CH_2Cl_2$  solution at  $-78^\circ C$ , as shown in Table 2.1

**Table 2.1** Relative rate of addition of bromine to alkenes

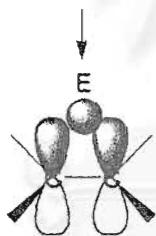
Alkene	Relative rate
$CH_2=CH_2$	1.0
$(CH_3)_2C=C(CH_3)_2$	14.0
$(CH_3)_2C=CHCH_3$	10.4
$(CH_3)_2C=CH_2$	5.53
$C_6H_5CH=CH_2$	3.35
$CH_3CH=CH_2$	2.03
$CH_3CH=CHCOOH$	0.26
$CH_2=CHBr$	0.04
$CH_2=CHCOOH$	0.03

## 2.4 Direction and stereochemistry of addition reactions

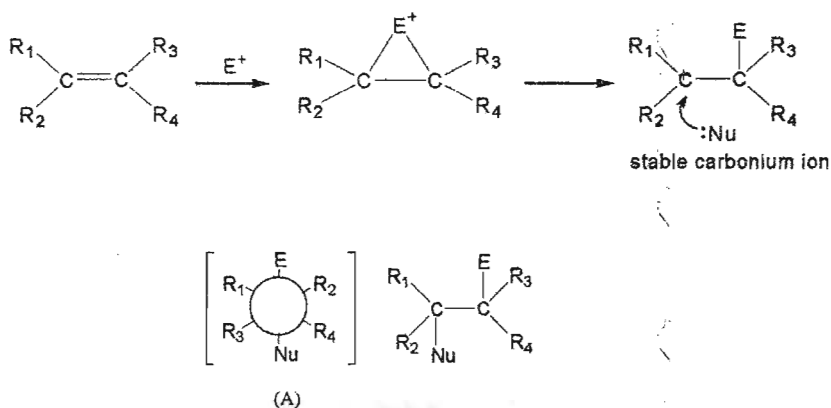
The configuration of the addition product can reasonably be ascertained by the consideration of three predictions:

- (1) The geometrical orientation of the two added substituents to each other and the rest of the molecule,
- (2) The choice as to which of the two doubly bond carbons is ultimately bonded to the positive part of the addendum and which to the nucleophilic part of the addendum in unsymmetrical double bonds, and
- (3) Which side of the double bond is attacked by the electrophile.

As the six atomic nuclei involved in a double bond of an alkene are all co-planar and the  $\pi$ -orbital is perpendicular to this plane on both the sides, the approach of the electrophile is also expected to be perpendicular to the plane of the alkene. The empty orbital of the electrophile comes in for bonding by overlapping with the  $\pi$ -orbital. The species formed by this initial overlap is called a  $\pi$ -complex (this may or may not be the actual intermediate) and may be represented as:



The  $\pi$ -complex or the three-membered ring intermediate is now roughly above the original plane of alkene and it must be opened by the attack of a nucleophile from below that plane. This amounts to an addition product with the nucleophile oriented in trans-position to the electrophilic atom and therefore the overall mechanism is trans-addition, which can be represented as:



The overall change in hybridization is from  $sp^2$  to  $sp^3$  for both the carbon atoms of the double bond and the resulting addition product is in the staggered conformation (A). One question still remains unanswered, i.e., which of the two doubly bond carbons is chosen for attack of the nucleophile after the formation of the  $\pi$ -complex. This may be decided by considering the bond-breaking in the  $\pi$ -complex (three-membered ring intermediate) as occurring at the carbon, which yields the most stable carbonium ion, followed by a direct nucleophilic attack from below. The transition state, therefore, has a lot of carbonium ion character and so the route via more stable carbonium ion (i.e., that having lower energy) is the energetically preferred one.

## 2.5 Oxidation reaction [8]

The practice and theory of oxidation processes have been developing over almost two centuries, and the scope of the subject is now extremely wide. Organic oxidation is briefly definable as loss of hydrogen or gain of oxygen by the substrate. It is applicable to virtually every type of carbon compound, and it variously takes the form of an addition, elimination, substitution, fission, coupling, or rearrangement process. Similarly, there is great diversity in the nature and behaviour of the oxidants employed in organic chemistry. They include some organic species as well as a very wide range of inorganic species. One-electron or two-electron transfer steps may be discerned in the oxidation-reduction process, and it often results in gain of hydrogen or loss of oxygen by the oxidant.

In cases under consideration, oxidation-reduction most commonly occurs between an organic and an inorganic compound in a solvent, and often in the presence of additional reagents or catalysts. An adequate understanding of such reactions requires knowledge of the parts played by all components of the system. Accordingly, oxidation provides one of the main areas in chemistry where the traditional separation of organic from inorganic topics is most rapidly disappearing.

The range of organic oxidation methods is continually enlarged by the introduction, often for specific types of reaction, of compounds not previously exploited for the purpose. Whereas, for example, the use of permanganate and chromic acid was established during the 19<sup>th</sup> century, and the appearance of selenium dioxide and periodate occurred in recent decades, the present review includes reference to ruthenium tetroxide, thallium(III) salts, palladium(II) salts, carbonium ions, and other oxidants, which have much more recently attracted attention. The scope of organic oxidation methods is also extendable by the use of particular techniques, exemplified in this review by photoactivation, heterogeneous and homogeneous catalysis, and electrolytic procedure.

In the present survey of oxidation methods, subdivisions have been made, as follows, in accordance with the different types of oxidants employed

1. Oxygen, and related reagents containing oxygen-oxygen bonds, i.e., ozone, and inorganic and organic peroxidic compounds.
2. Some non-metallic elements, oxides, and oxyanions, from positions neighbouring oxygen (Group V, VI, and VII) in the periodic table.
3. Salts, complexes, oxides, and oxyanions of transition and post-transition metals in their higher oxidation states. In the same section mention is made of some catalytic and electrolytic processes of oxidative type, which occur on metal surfaces.
4. Organic compounds capable of acting oxidatively, either by hydrogen abstraction or by oxygen-donation.



## 2.6 Sodium hypochlorite [9]

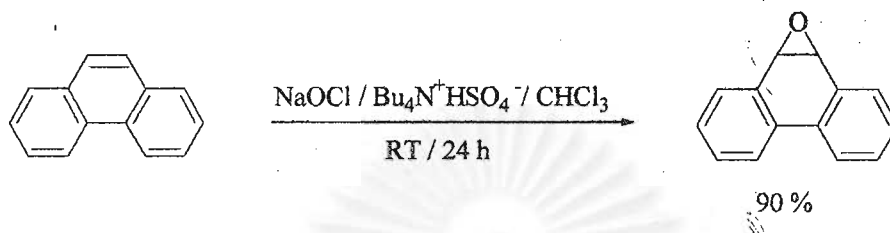
Sodium hypochlorite, a versatile and easily handled oxidizing agent, can oxidize alcohols, aldehydes, electron deficient alkenes, amines, and others. It is commercially available as aqueous solutions with 5.25-12.5% available chlorine (w/v) (0.74-1.75 M). Concentration is expressed in % available chlorine, since half of chlorine in bleach is present as NaCl. The pH of commercial bleach is typically 11-12.5, and it may be adjusted and buffered. The equilibrium composition of aqueous solutions of NaOCl is pH-dependent (eqs 1 and 2) and so pH control can be a critical consideration in many oxidation and chlorination reaction. Under strongly alkaline condition (pH>12), OCl<sup>-</sup> is the predominant form of positive chlorine. Because hypochlorite ion is insoluble in organic solvent, phase transfer catalysts are needed at this pH to effect oxidation reaction in biphasic media. In general, tetraalkylammonium salts have been the phase transfer catalysts of choice for such applications. Below pH 11, the equilibrium amount of HOCl becomes significant, and this form of positive chlorine is soluble in polar organic solvent such as CH<sub>2</sub>Cl<sub>2</sub>. No phase transfer catalysts is necessary to effect oxidation of substrates or catalysts dissolved in the organic phase of biphasic reaction in the pH range 10-11. Below pH 10, molecular chlorine becomes a significant component of aqueous bleach solutions, and the reactivity of these solutions can be attributed to that of Cl<sub>2</sub>.



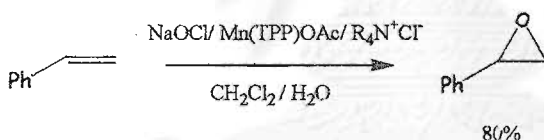
## 2.7 Literature reviews

Oxidation reactions are widely used in the synthesis because intermediates are important reactants for the functionalization of compounds. Sodium hypochlorite, a commodity chemical has gained a lot of attention in oxidation and halogenation reactions. It is simple, effective, cheap and easily available. Therefore, a lot of approaches have been reported on various reactions, which are listed as the following.

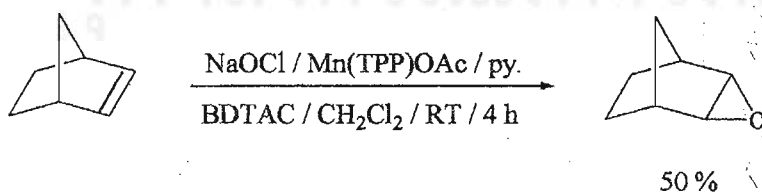
In 1977, Kuhn, D.G. et al. [10] used sodium hypochlorite (NaOCl) and tetrabutylammonium hydrogen sulfate in chloroform in the oxidation of phenanthrene for 24 hours. They used the mole ratio of substrate to NaOCl as high as 1:30. The oxidation of phenanthrene gave phenanthrene oxide in 90% yield.



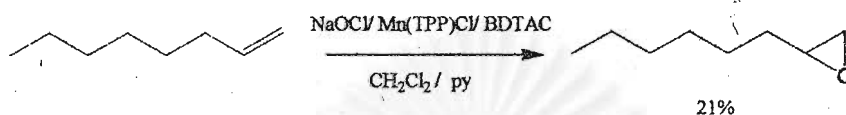
In 1980, Guilmet, E. et al. [11] used sodium hypochlorite (NaOCl), m-tetraphenylporphyrinatomanganese acetate (Mn(TPP)OAc), benzyldimethyltetradecyl ammonium chloride ( $\text{R}_4\text{N}^+\text{Cl}^-$ ) and  $\text{H}_2\text{O}$  in dichloromethane for oxidizing styrene at room-temperature for 3 hours. They used mole ratio of substrate to NaOCl as 1:1.75. The epoxidation of styrene gave styrene oxide in 80% yield.



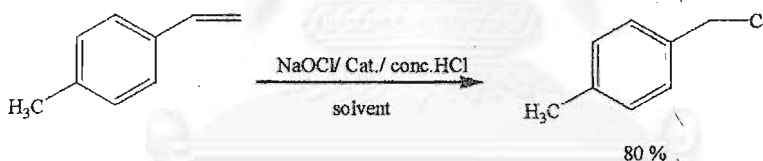
In 1984, Meunier, B. et al. [12] used sodium hypochlorite, m-tetraphenyl porphyrinatomanganese acetate (Mn(TPP)OAc), benzyldimethyltetradecylammonium chloride (BDTAC) and pyridine in dichloromethane for oxidizing norbornene for 4 hours. They used mole ratio of substrate to NaOCl as 1:1.75. The oxidation of norbornene gave norbornene oxide in 50% yield.



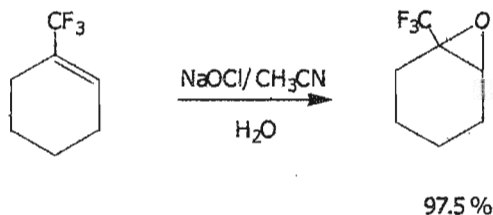
In the same year, Poorter, B.D. et al. [13] used sodium hypochlorite (NaOCl), meso-tetra (chlorophenyl)porphyrinatomanganese complex (Mn(TFPP)Cl), benzyltrimethylammoniumchloride (BDTAC) and pyridine in dichloromethane for oxidizing 1-octene at room-temperature for 3 hours. They used mole ratio of substrate to NaOCl as 1:2.5. The epoxidation of 1-octene gave 1-octene oxide in 21 %yield.



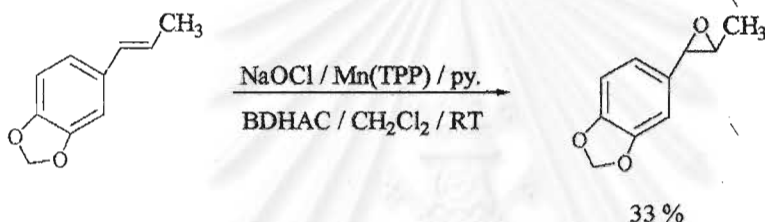
In 1989, Jones, R.G. et al. [14] used sodium hypochlorite (NaOCl), benzyltriethylammonium chloride and conc. HCl in chloroform/ dichloromethane mixture for oxidizing 4-methylstyrene at argon atmosphere for 1 hour. They used mole ratio of substrate to NaOCl as 1:5. The Chlorination of 4-methylstyrene gave 4-methylstyrene chloride in 80 %yield.



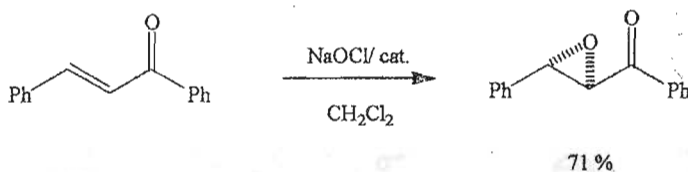
In 1990, Coe, P.L. et al. [15] used sodium hypochlorite (NaOCl), acetonitrile ( $\text{CH}_3\text{CN}$ ), and  $\text{H}_2\text{O}$  in the oxidation of 1-trifluoromethylnonafluoro cyclohex-1-ene at  $50^\circ\text{C}$  for 1 hour. They used mole ratio substrate to NaOCl as 1:2. The epoxidation of 1-trifluoromethylnonafluorocyclohex-1-ene gave 1-trifluoromethylnonafluoro-1, 2-epoxycyclohexane in 97.5 %yield.



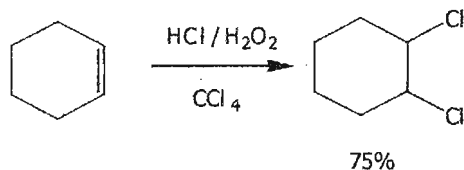
In 1996, Chiavetto, L. B. et al. [16] used sodium hypochlorite (NaOCl), m-tetraphenylporphyrinatomanganese (Mn(TPP)) and 4-methylbenzyltrimethylhexadecyl ammoniumchloride (BDHAC) in the oxidation of isosafrole in dichloromethane at room temperature. They used mole ratio of substrate to NaOCl as 1: 4. The oxidation of isosafrole gave isosafrole oxide in 33% yield.



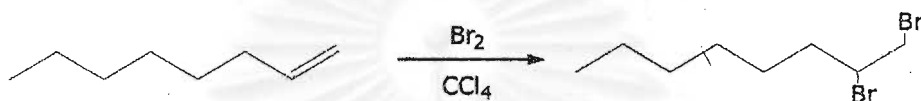
In 1999, Lygo, B. et al. [17] used sodium hypochlorite (NaOCl), N-anthracenylmethylcinchoninium chloride and dichloromethane in the oxidation of chalcone at 25°C for 48 hours. They used mole ratio of substrate to NaOCl as 1:2. The epoxidation of chalcone gave trans-2, 3-epoxy-1, 3-diphenylpropan-1-one in 71 % yield.



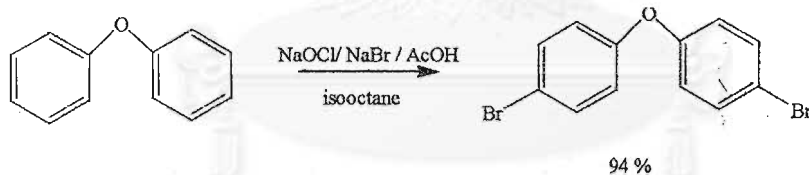
In the same year, Barhate, N.B. et al. [18] used hydrochloric acid, hydrogen peroxide and carbontetrachloride (CCl<sub>4</sub>) in the bromination of cyclohexene at room-temperature for 2 hours. They used mole ratio of substrate to H<sub>2</sub>O<sub>2</sub> as 1:2. The bromination of cyclohexene gave vic-dichlorocyclohexane in 75 % yield.



In the same year, Hardas, N.R. et, al. [19] used bromine ( $\text{Br}_2$ ) in carbontetrachloride ( $\text{CCl}_4$ ) in bromination of 1-octene at  $0^\circ\text{C}$  for 2 mins. They used mole ratio of substrate to  $\text{Br}_2$  as 1:2. The bromination of 1-octene gave 1, 2-dibromooctane.



In 2002, Kapuch, N. [6] used sodium hypochlorite ( $\text{NaOCl}$ ), sodium bromide ( $\text{NaBr}$ ), glacial acetic acid and isooctane in the bromination of diphenyl ether at room-temperature for 2 hours. The mole ratio of substrate to  $\text{NaOCl}$  was 1:16. The bromination of diphenyl ether gave 4, 4'-dibromodiphenyl ether in 94 %yield.



จุฬาลงกรณ์มหาวิทยาลัย

## CHAPTER III

### EXPERIMENTAL

#### 3.1 General methods

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck kieselgel 60 F<sub>254</sub>) and substances were detected using iodine vapour. The FT-IR spectra were recorded on a Nicolet Fourier Transformed Infrared Spectrophotometer model Impact 410. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained with a Bruker model ACF200 spectrometer, which operated at 200.13 MHz for <sup>1</sup>H and 50.32 MHz for <sup>13</sup>C nuclei. In all cases, samples were dissolved in deuterated chloroform and chemical shifts were recorded using a residual chloroform signal as an internal reference except indication of other deuterated solvents.

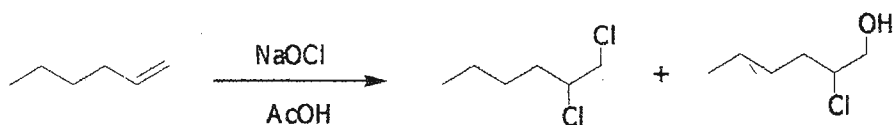
#### 3.2 Chemicals

Methyl methacrylate, sodium hypochlorite, cyclohexene, acetic acid, 1-hexene, 1, 5-hexadiene were purchased from Merck. Sodium bromide was obtained from BDH. Standard analytical grade reagents were used without further purification.

#### 3.3 Oxidative halogenation of 1-hexene

##### 1.) Effect of mole ratio of substrate and sodium bromide

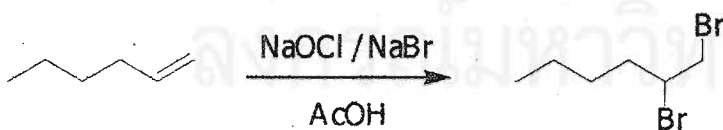
- 1.1) Oxidative halogenation of 1-hexene using 1/8 mole ratio of substrate and sodium hypochlorite (mixture 1H)



Glacial acetic acid (6 ml) was added into a 50 ml round bottom flask containing 1-hexene (0.42g, 5mmol). Then, sodium hypochlorite (18.72 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours at room temperature. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the oil product was extracted with 15 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as colorless liquid (0.19g, 45%) with  $R_f$  0.57 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 1H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.00 (3H, t), 1.50-2.10 (6H, m), 3.80 (2H, m), 4.10 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 22.1, 27.1, 34.7, 48.2, 61.2 (C,  $\text{C}_6\text{H}_{12}\text{Cl}_2$ ), 13.9, 22.1, 27.1, 34.7, 48.2, 72.8 (C,  $\text{C}_6\text{H}_{13}\text{OCl}$ ); **IR spectrum** ( $\text{NaCl}$  cell ( $\text{cm}^{-1}$ )): 2865 (C-H-stretching), 683 (C-Cl-stretching); **GC-MS chromatogram** ( $m/z$ ): 137 ( $t_R$ : 10.58 min;  $\text{C}_6\text{H}_{13}\text{OCl}$ ), 155 ( $t_R$ : 16.62 min;  $\text{C}_6\text{H}_{13}\text{OCl}$ ). Figures A 1-7.

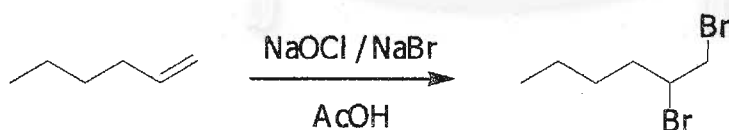
1.2) Oxidative halogenation of 1-hexene using 1/2.5 mole ratio of substrate and sodium bromide (mixture 2H)



Glacial acetic acid (6 ml) was added into a 50 ml round bottom flask containing sodium bromide (1.29g, 12.5mmol) and 1-hexene (0.42 g, 5mmol). Then, sodium hypochlorite (18.72 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the product was extracted with 15 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as a colorless liquid (0.25 g, 59%) with  $R_f$  0.47 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 2H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.98 (3H, t), 1.3-2.2 (6H, m), 3.60-3.82 (2H, m), 4.22 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 21.9, 28.9, 35.7, 36.4, 53.1 (C,  $\text{C}_6\text{H}_{12}\text{Br}_2$ ); **IR** spectrum (NaCl cell ( $\text{cm}^{-1}$ )): 2916 (C-H-stretching), 574 (C-Br-stretching), 647 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 244 ( $t_R$ : 10.73 min;  $\text{C}_6\text{H}_{12}\text{Br}_2$ ). Figures A 8-12.

1.3) Oxidative halogenation of 1-hexene using 1/5 mole ratio of substrate and sodium bromide (mixture 3H)

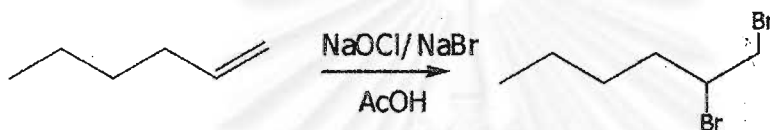


The same procedure as in the preparation of mixture 2H was followed, except sodium bromide (2.85 g, 25 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.32 g, 72%) with  $R_f$  0.45 (ethyl acetate: hexane (5:95)).



**Characteristic data for mixture 3H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.98 (3H, s), 1.12-2.24 (6H, m), 3.4-3.8 (2H, m), 4.02-4.23 (1H, m), 4.81-5.12 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 21.9, 28.8, 35.7, 36.4, 53.1 (C,  $\text{C}_6\text{H}_{12}\text{Br}_2$ ); **IR spectrum** ( $\text{NaCl}$  cell ( $\text{cm}^{-1}$ )): 2952 (CH-stretching), 575 (C-Br-stretching), 645 (C-Cl-stretching); **GC-MS chromatogram** ( $m/z$ ): 244 ( $t_R$ : 10.72 min;  $\text{C}_6\text{H}_{12}\text{Br}_2$ ). Figures A 13-17.

- 1.4) Oxidative halogenation of 1-hexene using 1/10 mole ratio of substrate and sodium bromide (mixture 4H)

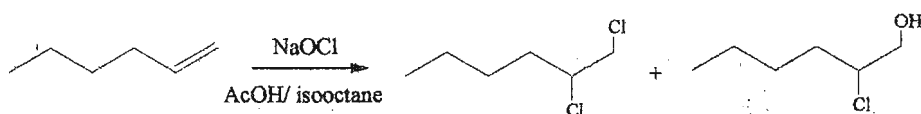


The same procedure as in the preparation of mixture 2H was followed, except sodium bromide (1.29 g, 12.5 mmol) was substituted with 5.7g of 50 mmol sodium bromide. The product was obtained as a colorless liquid (0.36 g, 85%) with  $R_f$  0.38 (ethyl: acetate (5:95)).

**Characteristic data for mixture 4H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.98 (3H, m), 1.26-2.24 (6H, m), 3.5-3.82 (2H, m), 4.22-4.35 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 21.9, 28.9, 35.7, 36.4, 53.1 (C,  $\text{C}_6\text{H}_{12}\text{Br}_2$ ); **IR spectrum** ( $\text{NaCl}$  cell ( $\text{cm}^{-1}$ )): 2915 (CH-stretching), 572 (C-Br-stretching), 645 (C-Cl-stretching); **GC-MS chromatogram** ( $m/z$ ): 244 ( $t_R$ : 10.73 min;  $\text{C}_6\text{H}_{12}\text{Br}_2$ ). Figures A 18-22.

## 2.) Effect of co-solvents

- 2.1 Oxidative halogenation of 1-hexene using 1/8 mole ratio of substrate and sodium hypochlorite (mixture 5H)



The same procedure as in the preparation of mixture 1H was followed, except that isooctane (8ml) was added into the solution. After usual workup, the product was obtained as a colorless liquid (0.26 g, 62%) with  $R_f$  0.46 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 5H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.78 (3H, m), 0.92-1.85 (6H, m), 3.01-3.42 (2H, m), 3.64-3.82 (1H, d), 4.62 (1H, s);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 22.1, 29.7, 31.3, 48.2, 61.2 (C,  $\text{C}_6\text{H}_{12}\text{Cl}_2$ ), 13.9, 22.1, 29.7, 34.7, 45.7, 72.8 (C,  $\text{C}_6\text{H}_{13}\text{OCl}$ ); **IR** spectrum (NaCl cell ( $\text{cm}^{-1}$ )): 2916 (C-H-stretching), 647 (C-Cl-stretching); **GC-MS** chromatogram (m/z): 137 ( $t_R$ : 10.59 min;  $\text{C}_6\text{H}_{13}\text{OCl}$ ), 155 ( $t_R$ : 16.61 min;  $\text{C}_6\text{H}_{12}\text{Cl}_2$ ). Figures A 23-28.

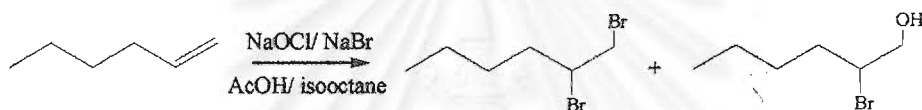
## 2.2 Oxidative halogenation of 1-hexene using 1/5 mole ratio of substrate and sodium bromide (mixture 6H)



The same procedure as in the preparation of mixture 2H was followed, except sodium bromide (2.58 g, 25 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.30 g, 71%) with  $R_f$  0.45 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 6H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.89 (3H, m), 1.09-2.22 (6H, m), 3.33-3.95 (2H, m), 4.19 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 21.9, 28.9, 31.5, 42.0, 72.8 (C,  $\text{C}_6\text{H}_{13}\text{OCl}$ ), 13.9, 21.9, 28.9, 35.7, 36.5, 53.1 (C,  $\text{C}_6\text{H}_{12}\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2923 (C-H-stretching), 581 (C-Br-stretching), 654 (C-Cl-stretching), **GC-MS chromatogram** (m/z): 244 ( $t_R$ : 10.71 min;  $\text{C}_6\text{H}_{12}\text{Br}_2$ ), 181 ( $t_R$ : 16.31 min;  $\text{C}_6\text{H}_{13}\text{OBr}$ ). Figures A29-34.

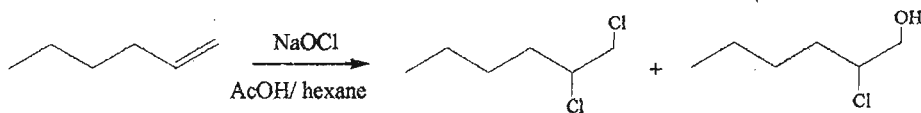
2.3 Oxidative halogenation of 1-hexene using 1/10 mole ratio of substrate and sodium bromide (mixture 7H)



The same procedure as in the preparation of mixture 2H was followed, except sodium bromide (5.7 g, 50 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.37 g, 88%) with  $R_f$  0.45 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 7H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.98 (3H, m), 1.24-2.23 (6H, m), 3.62-3.94 (2H, d), 4.18 (1H, s);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 21.9, 28.9, 31.5, 47.8, 76.6 (C,  $\text{C}_6\text{H}_{13}\text{OCl}$ ), 13.9, 21.9, 28.9, 35.7, 36.5, 53.1 (C,  $\text{C}_6\text{H}_{12}\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2959 (C-H-stretching), 574 (C-Br-stretching), 645 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 244 ( $t_R$ : 10.72 min;  $\text{C}_6\text{H}_{12}\text{Br}_2$ ), 181 ( $t_R$ : 16.31 min;  $\text{C}_6\text{H}_{13}\text{OBr}$ ). Figures A 35-40.

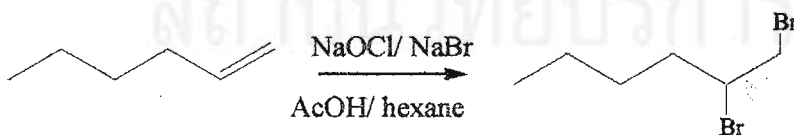
#### 2.4 Oxidative halogenation of 1-hexene using 1/8 mole ratio of substrate and sodium hypochlorite (mixture 8H)



The same procedure as in the preparation of mixture 5H was followed, except 8 ml of isooctane was substituted with 15 ml of hexane. The colorless oil of mixture 8H (0.25 g, 59%) was obtained with  $R_f$  0.56 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 8H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.84 (3H, m), 0.92-1.86 (6H, m), 3.19-3.62 (2H, 2), 3.84 (1H, s), 4.74 (1H, s);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 22.1, 27.9, 31.2, 48.2, 61.2 (C,  $\text{C}_6\text{H}_{12}\text{Cl}_2$ ), 13.9, 22.1, 29.7, 34.7, 45.7, 72.3 (C,  $\text{C}_6\text{H}_{13}\text{OCl}$ ); IR spectrum (NaCl cell ( $\text{cm}^{-1}$ )): 2862 (C-H-stretching), 618 (C-Cl-stretching); GC-MS chromatogram (m/z): 137 ( $t_R$ : 10.57 min;  $\text{C}_6\text{H}_{13}\text{OCl}$ ), 155 ( $t_R$ : 16.61 min;  $\text{C}_6\text{H}_{12}\text{Cl}_2$ ). Figures A 41-47.

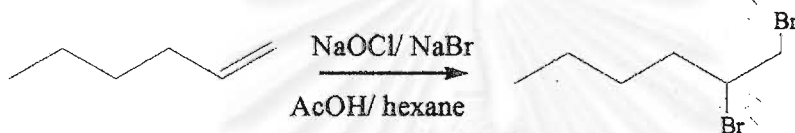
#### 2.5 Oxidative halogenation of 1-hexene using 1/5 mole ratio of substrate and sodium bromide (mixture 9H)



The same procedure as in the preparation of mixture 6H was followed, except 8 ml of isooctane was substituted with 15 ml of hexane. The colorless oil of mixture 9H (0.31 g, 76%) was obtained with  $R_f$  0.48 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 9H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 0.97 (3H, m), 1.24-2.31 (6H, m), 3.62-3.95 (2H, m), 4.35 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 21.9, 28.9, 35.7, 36.5, 53.1 (C,  $\text{C}_6\text{H}_{12}\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2930 (C-H-stretching), 581 (C-Br-stretching), 647 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 244 ( $t_{\text{R}}$ : 10.74 min;  $\text{C}_6\text{H}_{12}\text{Br}_2$ ). Figures A 48-52.

2.6 Oxidative halogenation of 1-hexene using 1/10 mole ratio of substrate and sodium bromide (mixture 10H)



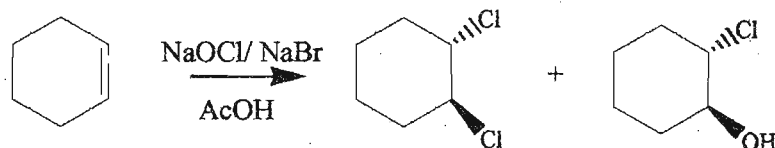
The same procedure as in the preparation of mixture 7H was followed, except 8 ml of isooctane was substituted by 15 ml of hexane. The colorless oil of mixture 10H (0.28 g, 69%) was obtained with  $R_f$  0.46 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 10H:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.02 (3H, m) 1.19-2.23 (6H, m), 3.6-3.94 (2H, m), 4.26 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 13.9, 21.9, 28.9, 35.7, 36.5, 53.1 (C,  $\text{C}_6\text{H}_{12}\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2923 (C-H-stretching), 589 (C-Br-stretching), 661 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 244 ( $t_{\text{R}}$ : 10.74 min;  $\text{C}_6\text{H}_{12}\text{Br}_2$ ). Figures A53-57.

## 2.) Oxidative halogenation of cyclohexene

### 1.) Effect of mole ratio of substrate and sodium bromide

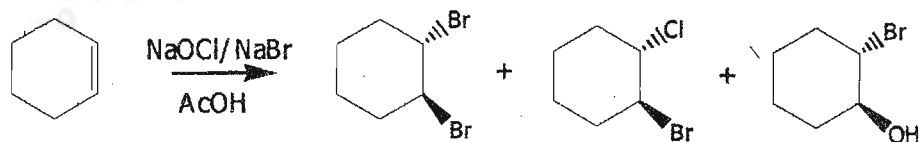
1.1 Oxidative halogenation of cyclohexene using 1/8 mole ratio of substrate and sodium hypochlorite (mixture 1C)



Glacial acetic acid (8 ml) was added into a 50 ml round bottom containing cyclohexene (0.82 g, 10 mmol). Then, sodium hypochlorite (37.44 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours at room-temperature. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the oil product was extracted with 5 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as a colorless liquid (0.36 g, 43%) with  $R_f$  0.38 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 1C:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.23-2.46 (8H, m), 3.65-3.84 (2H, m), 2.1 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 23.3, 34.9, 60.8 (C,  $\text{C}_6\text{H}_{10}\text{Cl}_2$ ), 21.1, 23.3, 24.6, 30.8, 60.8, 75.8 (C,  $\text{C}_6\text{H}_{11}\text{OCl}$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2952 (C-H-stretching), 618 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 153 ( $t_R$ : 9.34 min;  $\text{C}_6\text{H}_{10}\text{Cl}_2$ ), 135 ( $t_R$ : 11.82 min;  $\text{C}_6\text{H}_{11}\text{OCl}$ ). Figures B 1-7.

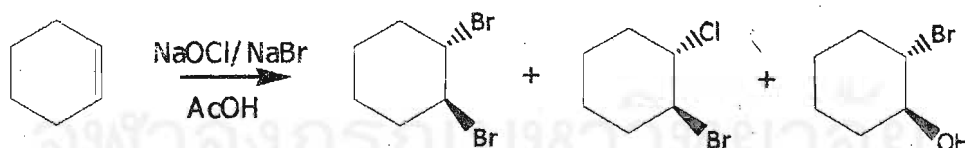
### 1.2 Oxidative halogenation of cyclohexene using 1/2.5 mole ratio of substrate and sodium bromide (mixture 2C)



Glacial acetic acid (8 ml) was added into 50 ml round bottom flask containing sodium bromide (2.58 g, 25 mmol) and of cyclohexene (0.82 g, 10 mmol). Then, sodium hypochlorite (37.44 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the oil product was extracted with 5 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as a colorless liquid (0.42 g, 53%) with  $R_f$  0.42 (ethyl acetate: hexane (5:95)).

**Characteristic data for mixture 2C:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.18-2.54 (8H, m), 4.18 (2H, s), 4.3 (2H, m), 2.1 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 22.4, 32.0, 55.2 (C,  $\text{C}_6\text{H}_{10}\text{Br}_2$ ), 22.4, 23.3, 32.1, 32.3, 55.2, 63.2 (C,  $\text{C}_6\text{H}_{10}\text{BrCl}$ ), 22.4, 23.4, 31.0, 32.0, 55.2, 76.0 (C,  $\text{C}_6\text{H}_{11}\text{OBr}$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2938 (C-H-stretching), 509 (C-Br-stretching), 603 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 198 ( $t_R$ : 10.75 min;  $\text{C}_6\text{H}_{10}\text{BrCl}$ ), 242 ( $t_R$ : 12.12 min;  $\text{C}_6\text{H}_{10}\text{Br}_2$ ), 179 ( $t_R$ : 21.01 min;  $\text{C}_6\text{H}_{11}\text{OBr}$ ). Figures B 8-13.

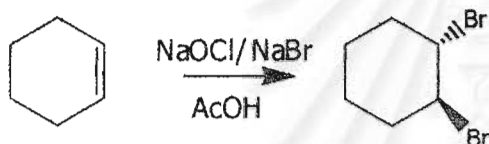
### 1.3 Oxidative halogenation of cyclohexene using 1/5 mole ratio of substrate and sodium bromide (mixture 3C)



The same procedure as in the preparation of mixture 2C was followed, except sodium bromide (5.15g of 50 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.37 g, 90%) with  $R_f$  0.39 (ethyl acetate: hexane (5: 95)).

**Characteristic data for mixture 3C:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.22-2.64 (8H, m), 4.20 (2H, m), 4.48 (2H, s), 2.1 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 22.4, 32.0, 55.2 (C,  $\text{C}_6\text{H}_{10}\text{Br}_2$ ), 22.4, 23.3, 32.0, 32.1, 55.2, 63.0 (C,  $\text{C}_6\text{H}_{10}\text{BrCl}$ ), 22.4, 23.4, 31.0, 32.0, 55.2, 76.0 (C,  $\text{C}_6\text{H}_{11}\text{OBr}$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2930 (C-H-stretching), 545 (C-Br-stretching), 690 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 198 ( $t_R$ : 10.75 min;  $\text{C}_6\text{H}_{10}\text{BrCl}$ ), 242 ( $t_R$ : 12.12 min;  $\text{C}_6\text{H}_{10}\text{Br}_2$ ), 179 ( $t_R$ : 12.96 min;  $\text{C}_6\text{H}_{11}\text{OBr}$ ). Figures B14-19.

#### 1.4 Oxidative halogenation of cyclohexene using 1/10 mole ratio of substrate and sodium bromide (mixture 4C)



The same procedure as in the preparation of mixture 2C was followed, except sodium bromide (10.30g of 100 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.35 g, 86%) with  $R_f$  0.42 (ethyl acetate: hexane (5:95)).

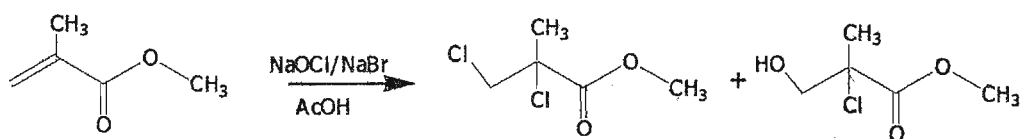
**Characteristic data for mixture 4C:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.32-2.53 (8H, m), 4.46 (2H, s);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 22.4, 32.0, 55.2 (C,  $\text{C}_6\text{H}_{10}\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2948 (CH-stretching), 582 (C-Br-stretching), 705 (C-Cl-stretching). Figures B 20-22.

### 3.) Oxidative halogenation of methylmethacrylate (MMA)

#### 1.) Effect of mole ratio of substrate and sodium bromide

##### 1.1 Oxidative halogenation of MMA using 1/8 mole ratio of substrate and sodium hypochlorite (mixture 1M)

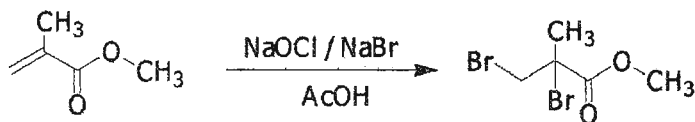




Glacial acetic acid (8 ml) was added into 50 ml round bottom flask containing MMA (1.00 g, 10 mmol). Then, sodium hypochlorite (37.44 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours at room-temperature. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the oil product was extracted with 5 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as a colorless liquid (0.68 g, 68%) with  $R_f$  0.35 (ethyl acetate: hexane (20:80)).

**Characteristic data for mixture 1M:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.87-2.25 (3H, m), 3.62-3.95 (3H, m), 4.19 (2H, m), 2.1 (1H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 21.0, 50.5, 52.8, 65.4, 169.1 (C,  $\text{C}_5\text{H}_8\text{O}_2\text{Cl}_2$ ), 19.2, 50.2, 65.7, 75.2, 169.1 (C,  $\text{C}_5\text{H}_9\text{O}_3\text{Cl}$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2945 (C-H-stretching), 640 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 153 ( $t_R$ : 10.20 min;  $\text{C}_5\text{H}_9\text{O}_3\text{Cl}$ ), 171 ( $t_R$ : 16.65 min;  $\text{C}_5\text{H}_8\text{O}_2\text{Cl}_2$ ). Figures C1-6.

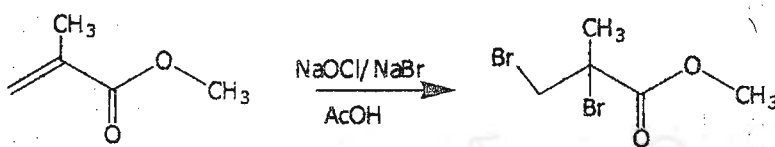
1.2 Oxidation of MMA using 1/2.5 mole ratio of substrate and sodium bromide (mixture 2M)



Glacial acetic acid (8 ml) was added into 50 ml round bottom flask containing sodium bromide (2.58 g, 25 mmol) and MMA (1.00 g, 10 mmol). Then, sodium hypochlorite (37.44 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the oil product was extracted with 5 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as a colorless liquid (0.72 g, 72%) with  $R_f$  0.38 (ethyl acetate: hexane (20: 80)).

**Characteristic data for mixture 2M:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.82-2.14 (3H, m), 3.52-3.71 (3H, m), 4.32 (2H, t);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 26.4, 38.1, 50.1, 53.5, 169.1 (C,  $\text{C}_5\text{H}_8\text{O}_2\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2952 (C-H-streching), 523 (C-Br-streching), 610 (C-Cl-streching); **GC-MS chromatogram** (m/z): 260 ( $t_R$ : 10.52 min;  $\text{C}_5\text{H}_8\text{O}_2\text{Br}_2$ ). Figures C 7-11.

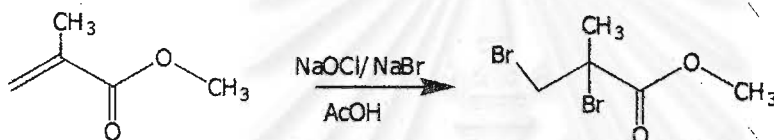
### 1.3 Oxidative halogenation of MMA using 1/5 mole ratio of substrate and sodium bromide (mixture 3M)



The same procedure as in the preparation of mixture 2M was followed, except sodium bromide (5.15 g of 50 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.48 g, 96%) with  $R_f$  0.37 (ethyl acetate: hexane (20:80)).

**Characteristic data for mixture 3M:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.94-2.10 (3H, m), 3.72-3.89 (3H, m), 4.2 (2H, t);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 26.4, 38.1, 50.1, 53.5, 169.1 (C,  $\text{C}_5\text{H}_8\text{O}_2\text{Br}_2$ ); **IR spectrum** ( $\text{NaCl}$  cell ( $\text{cm}^{-1}$ )): 2960 (C-H-stretching), 545 (C-Br-stretching), 647 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 260 ( $t_R$ : 10.50 min;  $\text{C}_5\text{H}_8\text{O}_2\text{Br}_2$ ). Figures C12-16.

1.4 Oxidative halogenation of MMA using 1/10 mole ratio of substrate and sodium bromide (mixture 4M)



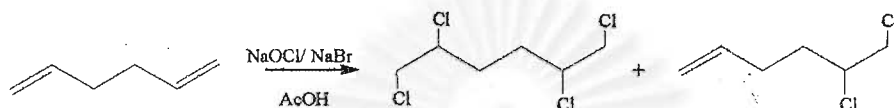
The same procedure as in the preparation of mixture 2M was followed, except sodium bromide (10.30g of 100 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.48 g, 96%) with  $R_f$  0.37 (ethyl acetate: hexane (20:80)).

**Characteristic data for mixture 4M:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.92-2.23 (3H, m), 3.81-3.92 (3H, m), 4.22 (2H, d);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 26.4, 38.1, 50.1, 53.5, 169.2 (C,  $\text{C}_5\text{H}_8\text{O}_2\text{Br}_2$ ); **IR spectrum** ( $\text{NaCl}$  cell ( $\text{cm}^{-1}$ )): 2950 (C-H-stretching), 562 (C-Br-stretching), 648 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 260 ( $t_R$ : 10.49 min;  $\text{C}_5\text{H}_8\text{O}_2\text{Br}_2$ ). Figures C17-21.

#### 4.) Oxidative halogenation of 1, 5-hexadiene

##### 1.) Effect of mole ratio of substrate and sodium bromide

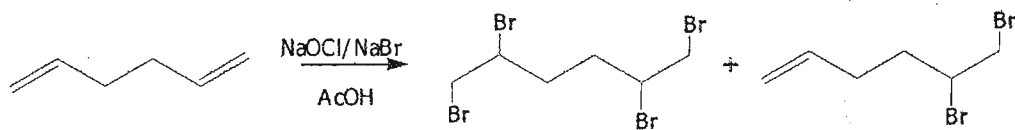
##### 1.1 Oxidative halogenation of 1, 5-hexadiene using 1/8 mole ratio of substrate and sodium hypochlorite (mixture 1HD)



Glacial acetic acid (8 ml) was added into a 50 ml round bottom flask and 1,5-hexadiene (0.82 g, 10 mmol). Then sodium hypochlorite (37.44 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours at room-temperature. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the oil product was extracted with 5 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as a colorless liquid (0.61g, 75%) with  $R_f$  0.45 (ethyl acetate: hexane (20:80)).

**Characteristic data for mixture 1HD:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.52-2.38 (4H, m), 3.42-3.95 (4H, m), 3.98-4.21 (2H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 31.7, 31.7, 47.8, 47.8, 59.8, 59.8 (C,  $\text{C}_6\text{H}_{10}\text{Cl}_4$ ); **IR spectrum** ( $\text{NaCl}$  cell ( $\text{cm}^{-1}$ )): 2923 (C-H-stretching), 632 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 224 ( $t_R$ : 14.62 min;  $\text{C}_6\text{H}_{10}\text{Cl}_4$ ), 153 ( $t_R$ : 16.11 min;  $\text{C}_6\text{H}_{10}\text{Cl}_2$ ). Figures D1-5.

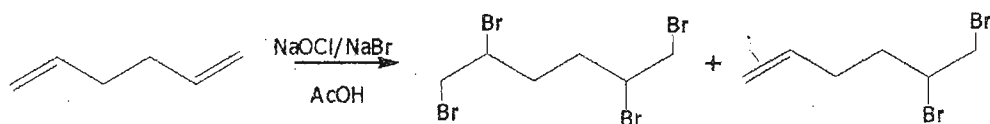
### 1.2 Oxidative halogenation of 1,5-hexadiene using 1/2.5 mole ratio of substrate and sodium bromide (mixture 2HD)



Glacial acetic acid (8 ml) was added into a 50 ml round bottom flask containing sodium bromide (2.58 g, 25 mmol) to and 1, 5-hexadiene (0.82 g, 10mmol). Then, sodium hypochlorite (37.44 ml, 2M) was added very slowly using a dropping-funnel into the mixture and stirred for 3 hours. The mixture was neutralised with 3M sodium hydroxide. The two phases were separated using a separating-funnel, then the oil product was extracted with 15 ml of hexane (3x5 ml) and washed 4-5 times with water. The combined organic layer was dried over sodium sulfate anhydrous and filtered. Hexane was removed by evaporation and the product was obtained as a colorless liquid (0.52 g, 63%) with  $R_f$  0.38 (ethyl acetate: hexane (20:80)).

**Characteristic data for mixture 2HD:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): (H,  $\text{C}_6\text{H}_{10}\text{Br}_2$ ) 1.76-2.75 (4H, m), 3.41-4.0 (4H, m), 4.0-4.4 (2H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 33.5, 33.5, 35.7, 35.7, 51.5, 51.5 ( $\text{C}, \text{C}_6\text{H}_{10}\text{Br}_2$ ); **IR spectrum** ( $\text{NaCl}$  cell ( $\text{cm}^{-1}$ )): 2925 (C-H-streching), 582 (C-Br-streching), 648 (C-Cl-streching); **GC-MS chromatogram** (m/z): 242 ( $t_R$ : 17.84 min;  $\text{C}_6\text{H}_{10}\text{Br}_2$ ), 402 ( $t_R$ : 18.91 min;  $\text{C}_6\text{H}_8\text{Br}_4$ ). Figures D6-10.

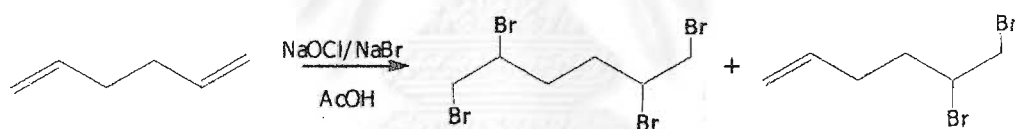
### 1.3 Oxidative halogenation of 1,5-hexadiene using 1/5 mole ratio of substrate and sodium bromide (mixture 3HD)



The same procedure as in the preparation of mixture 2HD was followed, except sodium bromide (5.15 g, 50 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.34 g, 82%) with  $R_f$  0.38 (ethyl acetate: hexane (20:80)).

**Characteristic data for mixture 3HD:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.82-2.61 (4H, m), 3.48-4.01 (4H, m), 4.05-4.23 (2H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 33.5, 33.5, 35.8, 35.8, 51.6, 51.6 (C,  $\text{C}_6\text{H}_{10}\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2924 (C-H-stretching), 581 (C-Br-stretching), 647 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 402 ( $t_R$ : 18.91 min;  $\text{C}_6\text{H}_9\text{Br}_4$ ), 242 ( $t_R$ : 17.84 min;  $\text{C}_6\text{H}_{10}\text{Br}_2$ ). Figures D11-15.

1.4 Oxidative halogenation of 1,5-hexadiene using 1/10 mole ratio of substrate and sodium bromide (mixture 4HD)



The same procedure as in the preparation of mixture 2HD was followed, except sodium bromide (10.30 g 100 mmol) was included in the reaction mixture. The product was obtained as a colorless liquid (0.64 g, 80%) with  $R_f$  0.36 (ethyl acetate: hexane (20:80)).

**Characteristic data for mixture 4HD:**  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 200MHz): 1.82-2.70 (4H, m), 3.41-4.05 (4H, m), 4.02-4.41 (2H, m);  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ , (ppm), 50MHz): 33.5, 33.5, 35.7, 35.7, 51.5, 51.5 (C,  $\text{C}_6\text{H}_{10}\text{Br}_2$ ); **IR spectrum** (NaCl cell ( $\text{cm}^{-1}$ )): 2930 (C-H-stretching), 585 (C-Br-stretching), 649 (C-Cl-stretching); **GC-MS chromatogram** (m/z): 402 ( $t_R$ : 18.93 min;  $\text{C}_6\text{H}_9\text{Br}_4$ ), 242 ( $t_R$ : 17.83 min;  $\text{C}_6\text{H}_{10}\text{Br}_2$ ). Figures D16-20.

## 5. Characterization of reaction products:

The reaction products were characterized using the follow spectroscopic techniques

1. Fourier-Transform Infrared Spectrophotometer (FT-IR)
2.  $^1\text{H}$  and  $^{13}\text{C}$  Nuclear Magnetic Resonance spectrometer (NMR)
3. Gas Chromatography-Mass spectrometer (GC-MS)

Gas chromatograph-mass spectrometer was used to identify and quantitatively determination of the mixture. The GC-MS was performed using DB5 capillary column. The general condition can be summarized as follows:

- Column** : DB5 MS (30m.)  
**Injection** : split 1:50 250°C  
**Carrier** : He at 24 cm<sup>3</sup>/min  
**Oven** : 60°C for 3 min  
60°C-220°C at 10°C/min  
220°C for 5 min

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

## CHAPTER IV

### RESULT AND DISCUSSION

The main purpose of this research is focused on the oxidative halogenation of alkene in order to avoid handling chlorine gas and liquid bromine. Sodium hypochlorite under acetic acid condition was studied and utilized for the halogenation process. The reagent is innovative, safe and easy to use.

The idea of this reagent come from the fact that NaOCl generates  $\text{Cl}_2$  in acidic medium. Thus NaOCl in glacial acetic acid should be able to generate available and controllable chlorine [6].

Many organic compounds can dissolve very well in glacial acetic acid. Therefore, glacial acetic acid has the dual purposes as acidity adjustment and solvent as well.

Reaction of gaseous chlorine or HOCl with bromide ion generates bromine in which bromine in glacial acetic acid is a known reagent for bromination, both addition and electrophilic aromatic substitution. Therefore, appropriate amount of bromide ion could determine the products outcome whether they are dichloro compounds, dibromo compounds or the mixture thereof. Thus the ratio of substrate, NaOCl and NaBr should be varied in order to gain more insight about reaction conditions.

It is known from the previous report [6] that solvent has certain effect on the course of the reaction. Therefore, isooctane and hexane are used as co-solvent for this oxidative halogenation reaction.

As a model compound, 1-hexene was selected as a substrate for suitable conditions. Thereafter, these reaction conditions were applied to 1,5-hexadiene, cyclohexene and methylmethacrylate. Thus some clues on substrate variation should be realized.

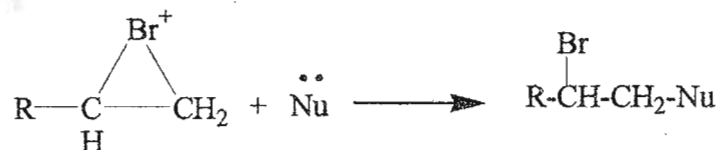
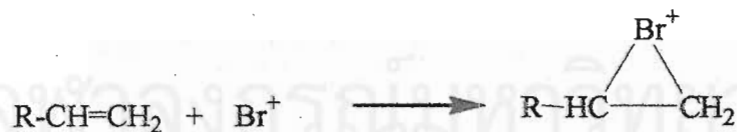
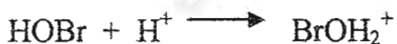


The proposed mechanism for oxidative halogenation of alkene is shown as the following:

*The mechanism of chlorination [20]*



*The mechanism of bromination [21]*



#### 4.1 Oxidative halogenation of 1-hexene

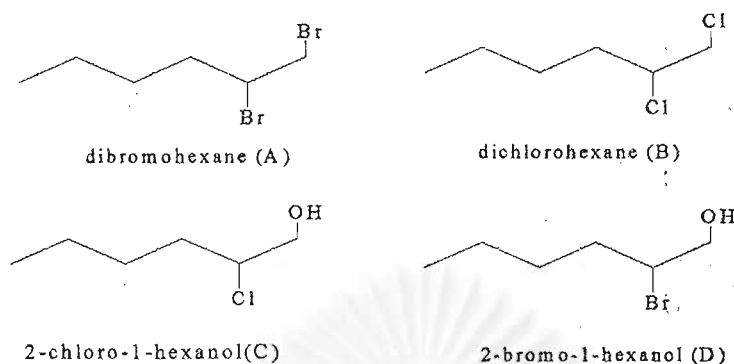
Oxidative halogenation of 1-hexene was expected to give dihalohexane derivatives. Under various conditions, halogenation products of 1-hexene are shown in Table 4.1 and Figure 4.1.

**Table 4.1** Oxidative halogenation of 1-hexene

Entry	Solvent	Mole ratio			% composition				
		substate	NaOCl	NaBr	A	B	C	D	uniden tified
1H	no extra solvent	1	8	0	-	31	29	-	40
2H	no extra solvent	1	8	2.5	94	-	-	-	6
3H	no extra solvent	1	8	5	90	-	-	-	10
4H	no extra solvent	1	8	10	100	-	-	-	-
5H	isooctane	1	8	0	-	10	70	-	20
6H	isooctane	1	8	5	46	-	-	54	-
7H	isooctane	1	8	10	79	-	-	21	-
8H	hexane	1	8	0	-	20	52	-	28
9H	hexane	1	8	5	100	-	-	-	-
10H	hexane	1	8	10	90	-	-	-	10

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

Halogenation products of 1-hexene derivatives are shown in figure 4.1



**Figure 4.1** The structures of hexane derivatives

From Table 4.1, reaction of 1-hexene with NaOCl in glacial acetic acid gave exclusively 1, 2-dichlorohexane (entry 1H). On the other hand, the same reaction in the presence of excess NaBr, 1,2-dibromohexane was exclusively obtained (entry 4H). Increasing ratio of substrate: NaBr from 1:1 to 1:5 gave, as expected, a mixture of haloalcohol (entry 6H). Therefore, synthetic application of this oxidative halogenation would be useful by controlling the reaction condition to get exclusively a dichloroalkane or a dibromoalkane.

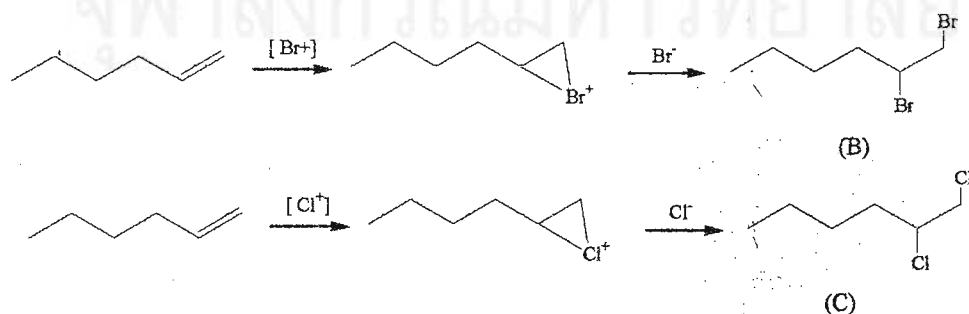
It was found that co-solvents did not show any significant improvement of the product yield. Therefore co-solvent could be eliminated from this reaction. However, in case of solubility problem of substrate a co-solvent could be used.

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

**Table 4.2** Simple normalization-integrator of GC-MS in the group of cyclohexene derivatives

Mixture	$t_R$ (min)	Molecular weight	Product
1H	10.58	137	Chlorohexanol
	16.62	155	Dichlorohexane
2H	10.73	244	Dibromohexane
3H	10.72	244	Dibromohexane
4H	10.73	244	Dibromohexane
5H	10.59	137	Chlorohexanol
	16.61	155	Dichlorohexane
6H	10.71	244	Dibromohexane
	16.31	181	Bromohexanol
7H	10.72	244	Dibromohexane
	16.31	181	Bromohexane
8H	10.57	137	Chlorohexanol
	16.61	155	Dichlorohexane
9H	10.74	244	Dibromohexane
10H	10.74	244	Dibromohexane

Mechanism of this oxidative halogenation could be proposed as the formation of halonium ion in the intermediate step with subsequent undergoes nucleophilic substitution with nucleophilic ( $\text{Cl}^-$  or  $\text{Br}^-$  or  $\text{AcO}^-$ ) to yield the corresponding products as shown in Figure 4.2.



**Figure 4.2** Mechanism of halogenation

The comparison of this method with that using potassium bromide (KBr) and cerium (IV) ammonium nitrate (CAN) method [1] is shown in Table 4.3.

**Table 4.3** Comparison of the oxidative bromination of 1-hexene using NaOCl/ NaBr and KBr/ CAN

Method	NaOCl/ NaBr		KBr/ CAN
Temperature	Room-Temperature		Room-Temperature
Reaction times	3 hours		20 min
Solvent	none	isooctane	dichloromethane
"Br" ratio	10	10	2
Yield	90	79	82

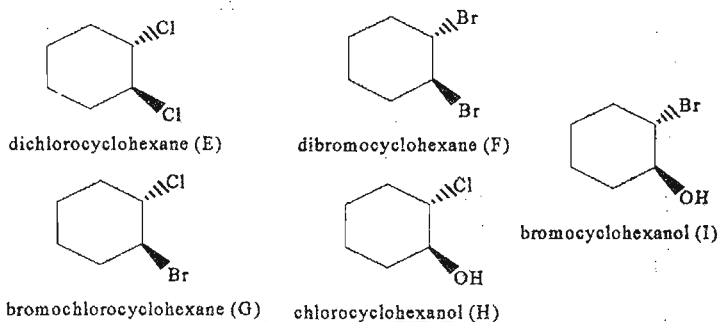
#### 4.2 Oxidative halogenation of cyclohexene

In case of cyclohexene, the products are tabulated in Table 4.4 and Figure 4.3. Basically, the relevant dihalocompounds were obtained similar to those of 1-hexene substrate. However, in case of cyclohexene, the stereochemistry was applied. It was found that the reaction products were *trans*-dihalocompounds which agree well with the halonium intermediate mechanism.

**Table 4.4** Oxidative halogenation of cyclohexene derivatives

Entry	Mole ratio			% composition					
	substrate	NaOCl	NaBr	E	F	G	H	I	unidentified
1C	1	8	0	6	-	-	70	-	24
2C	1	8	2.5	-	58	29	-	11	-
3C	1	8	5	-	57	15	-	19	-
4C	1	8	10	-	94	-	-	-	-

Halogenation products of cyclohexane derivatives are shown in figure 4.3



**Figure 4.3** The structure of cyclohexane derivatives

From Table 4.4, reaction of cyclohexene with NaOCl in glacial acetic acid gave exclusively 1, 2-dichlorocyclohexane and chlorocyclohexanol (entry 1C). On the other hand, the same reaction in the presence of excess NaBr, 1,2-dibromocyclohexane was exclusively obtained (entry 4C). Increasing ratio of substrate: NaBr from 1:1 to 1:5 gave, as expected, a mixture of halocyclohexanol and dihalocyclohexane (entry 2C and 3C). Therefore, synthetic application of this oxidative halogenation would be useful by controlling the reaction condition to get exclusively a dichloroalkane or a dibromoalkane.

**Table 4.5** Simple normalization-integrator of GC-MS in the group of cyclohexene derivatives

Mixture	$t_R$ (min)	Molecular weight	Products
1C	9.34	153	Dichlorocyclohexane
	11.82	135	Chlorocyclohexanol
2C	10.75	198	Bromochlorocyclohexane
	12.12	242	Dibromocyclohexane
	21.01	179	Bromocyclohexanol
3C	10.75	198	Bromochlorocyclohexane
	12.12	242	Dibromocyclohexane
	12.96	179	Bromocyclohexanol

The comparison of this method with that using potassium bromide (KBr) in cerium (IV) ammonium nitrate (CAN) method [1] and hydrobromic acid (HBr) in hydrogenperoxide (H<sub>2</sub>O<sub>2</sub>) method [18] is shown in Table 4.6.

**Table 4.6** Comparison of the oxidative bromination of cyclohexene using NaOCl/NaBr and other methods

Method	NaOCl/ NaBr	HBr/ H <sub>2</sub> O <sub>2</sub> [18]	KBr/ CAN/ H <sub>2</sub> O [1]
Temperature	Room-temperature	0°C	Room-temperature
Reaction times	3 hour	2 hour	20 min
Catalyst	none	none	CAN
Solvent	none	CCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>
"Br" ratio	10	2	2
Yield	94	86	65

### 4.3 Oxidative halogenation of methyl methacrylate (MMA)

To see the effect of electron withdrawing group on the double bond, the unsaturated ester, methylmethacrylate was used as a substrate. The results are shown in Table 4.7 and Figure 4.4.

**Table 4.7** Oxidative halogenation of MMA derivatives

Entry	Mole ratio			% composition			
	substrate	NaOCl	NaBr	J	K	L	unidentified
1M	1	8	0	12	-	88	-
2M	1	8	2.5	-	62	-	38
3M	1	8	5	-	61	-	39
4M	1	8	10	-	87	-	13

Halogenation products of methylmethacrylate derivatives are shown in figure

4.4.

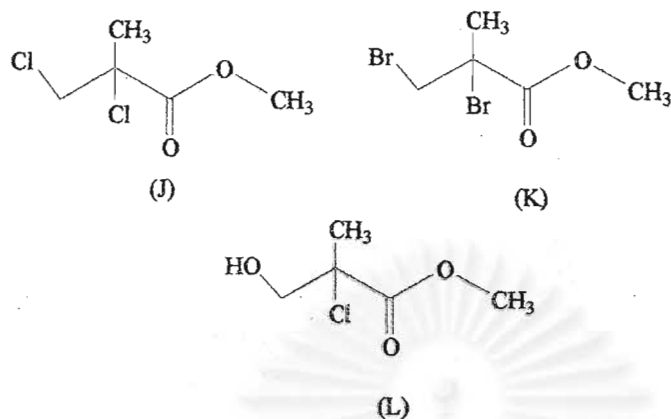


Figure 4.4 The structures of MMA derivatives

From Table 4.7, reaction of methylmethacrylate with NaOCl in glacial acetic acid gave exclusively 1, 2-dichlorocompound and chlorohydrincompound (entry 1M). On the other hand, the same reaction in the presence of excess NaBr, 1,2-dibromocompound was exclusively obtained (entry 4M).

Table 4.8 Simple normalization-integrator of GC-MS in the group of MMA derivatives

Mixture	$t_R$ (min)	Molecular weight	Products
1M	10.20	153	$C_5H_9O_3Cl$
	16.65	171	$C_5H_8O_2Cl_2$
2M	10.52	260	$C_5H_8O_2Br_2$
3M	10.50	260	$C_5H_8O_2Br_2$
4M	10.49	260	$C_5H_8O_2Br_2$



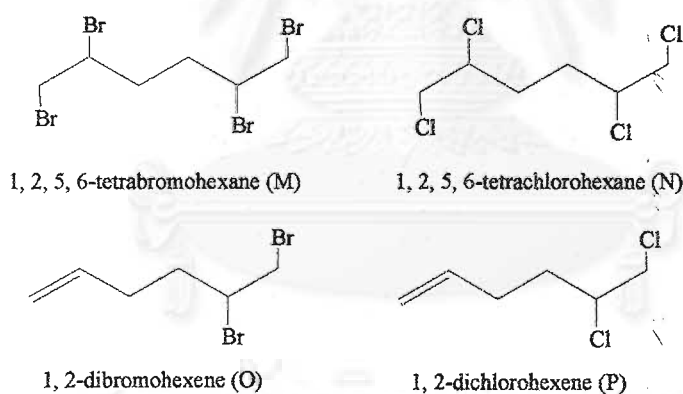
#### 4.4 Oxidative halogenation of 1, 5-hexadiene

To see the effect of diene, 1, 5-hexadiene was used as a substrate. The results are tabulated in Table 4.9 and in Figure 4.6.

**Table 4.9** Oxidative halogenation of 1, 5-hexadiene

Entry	Mole ratio			% composition				
	substrate	NaOCl	NaBr	M	N	O	P	unidentified
1HD	1	8	0	-	37	-	48	15
2HD	1	8	2.5	31	-	40	-	29
3HD	1	8	5	56	-	31	-	13
4HD	1	8	10	75	-	23	-	2

Halogenation products of 1, 5-hexadiene derivatives are shown in figure 4.5.



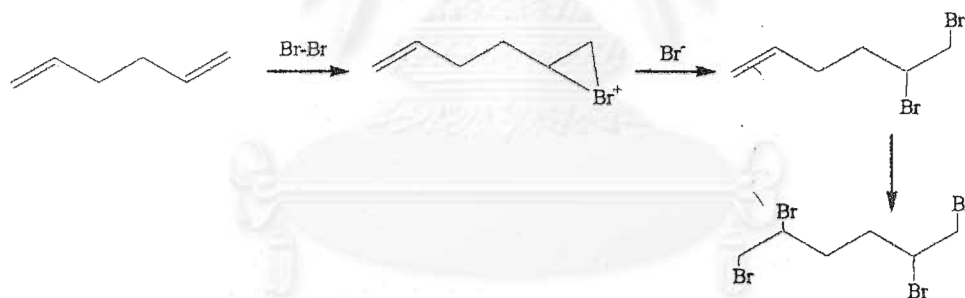
**Figure 4.5** The structures of 1, 5-hexadiene and its derivatives

From Table 4.9, reaction of 1, 5-hexadiene with NaOCl in glacial acetic acid gave exclusively 1, 2, 5, 6-tetrachlorohexane and 1, 2-dichlorohexene (entry 1HD). On the other hand, the same reaction in the presence of excess NaBr, 1, 2, 5, 6-tetrabromohexane and 1,2-dibromohexene were exclusively obtained (entry 4HD).

**Table 4.10** Simple normalization-integrator of GC-MS in the group of 1, 5-hexadiene derivatives

Mixture	$t_R$ (min)	Molecular weight	Products
1HD	14.63	224	1, 2, 5, 6-tetrachlorohexane
	16.17	153	1, 2-dichlorohexene
2HD	17.84	242	1, 2-dibromohexene
	18.91	402	1, 2, 5, 6-tetrabromohexane
3HD	17.84	242	1, 2-dibromohexene
	18.93	402	1, 2, 5, 6-tetrabromohexane
4HD	17.83	242	1, 2-dibromohexene
	18.93	402	1, 2, 5, 6-tetrabromohexane

The reaction mechanism was proposed below:



**Figure 4.6** Mechanism of tetrabromoalkane

It was interesting to compare this halogenation method using 1, 5-hexadiene with other relevant methods as shown in Table 4.11 [18]. Under our reaction condition, the yield of dibromocompound was quite high.

**Table 4.11** Comparison of bromination of dialkenes using NaOCl/ NaBr with other methods

Method	NaOCl/ NaBr	HBr/ H <sub>2</sub> O <sub>2</sub> [18]	
Substrate	1,5-hexadiene	Z,Z-1,5-cyclooctadiene	
Solvent	none	MeOH	CCl <sub>4</sub>
Temperature	Room-Temperature	0°C	0°C
Reaction times	3 hour	2 hour	2 hour
"Br" amount	5	2	2
Yield	57	26	84

#### 4.5 The effect of mole ratio of 1-hexene and sodium bromide

The oxidative halogenation of 1-hexene producing dibromohexane as a model product was studied. Various mole ratios of 1-hexene and sodium bromide such as 1:1, 1:2.5, 1:5, 1:10 were studied using mole ratio of 1-hexene and sodium hypochlorite at 1:8. % Yield of hexane derivatives is shown in Table 4.12.

**Table 4.12** The % yield of 1-hexene derivatives

Mole ratio	% yield of dibromohexane
1:8:2.5	100
1:8:5	90
1:8:10	94

From the result above, the mole ratio of 1-hexene: NaOCl: NaBr at 1:8:2.5 gave exclusive dibromohexane.

## CHAPTER V

### CONCLUSION

Sodium hypochlorite in acetic acid was utilized for the halogenation process. The reagent is safe and easy to use.

This research using 1-hexene, 1, 5-hexadiene, cyclohexene and methyl methacrylate as substrates using sodium hypochlorite, sodium bromide and glacial acetic acid combination as reactant

The oxidative halogenation of 1-hexene using mole ratio of substrate, sodium hypochlorite and sodium bromide as 1:8:10 and reaction times for 3 hours gave 90 % dibromohexane. If sodium bromide was omitted, 12% dichlorohexane was obtained. However, a mixture of product was obtained if the mole ratio of reactant is between 1:8:0 – 1:8:10.

The oxidative halogenation of 1-hexene producing dibromohexane as a model product was studied. Various mole ratios of 1-hexene and sodium bromide such as 1:2.5, 1:5, 1:10 were studied using mole ratio of 1-hexene and sodium hypochlorite as 1:8. The mole ratio of 1-hexene: NaOCl: NaBr at 1:8: 10 gave exclusively dibromohexane. However, at lower ratio of bromide, other products such as dichlorohexane and bromohexanol formed as well.

It was found that co-solvents did not show any significant improvement of the product yield. Therefore co-solvent could be eliminated from this reaction. However, in case of solubility problem of substrate a co-solvent such as hexane and isooctane could be used.

The oxidative halogenation of 1, 5-hexadiene using mole ratio of substrate, sodium hypochlorite and sodium bromide at 1:8:10 and reaction times for 3 hours gave 76 % 1, 2, 5, 6, tetrabromohexane.

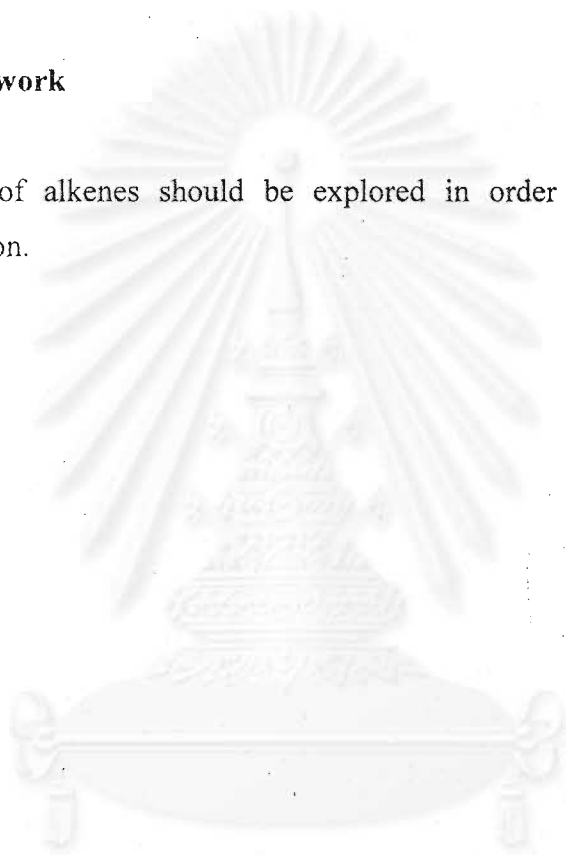
The oxidative halogenation of cyclohexene using mole ratio of substrate, sodium hypochlorite and sodium bromide at 1:8:10 and reaction times for 3 hours gave 94 % dibromocyclohexane.

The oxidative halogenation of methylmethacrylate using mole ratio of substrate, sodium hypochlorite and sodium bromide at 1:8:10 and reaction times for 3 hours gave 87% dibromoderivative.

From this study, it could be concluded that oxidative halogenation of alkene using a mixture of sodium hypochlorite, acetic acid and sodium bromide is synthetically useful. The products could be obtained in good yield. The products could be dichloroalkane, dibromoalkane or the mixture of chlorobromoalkane depends on the amount of bromide use. For synthetic applications, more than 5-fold excess of bromide gave exclusively the dibromoalkane.

#### **Suggestion for future work**

Various types of alkenes should be explored in order to determine the generality of this reaction.



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

## References

1. Nair, V.; Panicker, S.B., "An efficient bromination of alkenes using cerium (IV) ammonium nitrate (CAN) and potassium bromide" *Tetrahedron*. **2001**, *57*, 7417-7422.
2. Roy, S.C.; Guin, C., "An efficient chemo and regioselective oxidative nuclear bromination of activated aromatic compounds using lithium bromide and ceric ammonium nitrate" *Tetrahedron Lett.* **2001**, *42*, 6941-6942.
3. Metsger, L.; Bittner, S., "Autocatalytic oxidation of ethers with sodium bromate" *Tetrahedron*. **2000**, *56*, 1905-1910.
4. Roche, D.; Prasad, K.; "Mild and regioselective oxidative bromination of anilines using potassium bromide and sodium perborate" *Tetrahedron Lett.* **2000**, *41*, 2083-2085.
5. Kent, J.A. *Handbook of Industrial Chemistry a Brief Course*. 3<sup>rd</sup>ed. New York McGraw-Hill, **2002**, 163-177.
6. Kapuch, N., "Bromination of Aromatic Compounds Using Sodium bromide/ Sodium hypochlorite" *Master's Thesis*, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, **2002**.
7. Parmaar, V.S.; Chawla, H.W. *Principle of Reaction Mechanism in Organic Chemistry*. Delhi: Sultan Chand & Son, **1973**. 248-255.
8. Timmons, C.J.; *Modern Reaction in Organic Synthesis*. New York: Van Nostrand Reinhold Company, **1970**, 54-55.
9. Burke, S.D.; Danheiser, R.L. *Handbook of Reagents for Organic Synthesis* "Oxidizing and Reducing Agents" New York: John Wiley & Son, **1999**, 407-412.
10. Kuhn, D.G.; Hamilton, G.A., "Direct Oxidation in High Yield of Some Polycyclic Aromatic Compounds to Arene Oxides Using Hypochlorite and Phase Transfer Catalysts." *J. Am. Chem. Soc.* **1977**, *99*, 8121-8123.
11. Guilmet, E.; Meunier, B., "A New Catalytic Route for The Epoxidation of Styrene with Sodium Hypochlorite Activated by Transition Metal Complex" *Tetrahedron Lett.* **1980**, *21*, 4449-4450.

12. Meunier, B.; Guilmet, E., "Sodium Hypochlorite: A Convenient Oxygen Source for Olefin Epoxidation Catalyzed by ( Porphyrinato ) Manganese Complexes." *J. Am. Chem. Soc.* **1984**, *106*, 6668-6676.
13. Poorter, B. D.; Meunier, B., "Catalytic Epoxidation of Aliphatic Terminal Olefins with Sodium Hypochlorite" *Tetrahedron Lett.* **1984**, *25*(18), 1895-1896.
14. Jones, R.G.; Matsubayashi, Y., "Phase-transfer-catalysed Chlorination of Poly(4-methylstyrene) by Hypochlorite" *Polymer*, **1989**, *31*, 1519-1525.
15. Coe, L.P.; Mott, A.W., "Polyfluoro-1, 2-epoxy-alkenes and -cycloalkanes. Part VI. The synthesis and Some Reactions of 1-Trifluoromethylnonafluoro-1, 2-epoxycyclohexane" *J. Flu. Chem.* **1990**, *49*, 21-31.
16. Chiavetto, L.B.; Guglielmetti, G., "Oxidation of Isosafrol by Sodium Hypochlorite Catalysed by Manganese Porphyrins: Unusual Competition between Epoxidation and O - Dealkylation." *Tetrahedron Lett.* **1996**, *37*, 1091-1094.
17. Lygo, B.; Wainwright, P.G., "Phase-Transfer Catalysed Asymmetric Epoxidation of Enones using N-Anthracenylmethyl-Substituted Cinchona Alkaloids" *Tetrahedron*, **1999**, *55*, 6289-6300.
18. Barhate, N.B., Gajare, A.S., "Simple and Practical Halogenation of Arenes, Alkenes and Alkynes with Hydrohalic Acid/H<sub>2</sub>O<sub>2</sub> (or TBHP)" *Tetrahedron*. **1999**, *55*, 11127-11142.
19. Hardas, N.R.; Adam, R., "Alkene determination and gas chromatography with element-selective atomic plasma spectroscopic detection" *J. Chromatography A.* **1999**, *884*, 249-258.
20. Mare, D.L. "The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part I" *J. Chem. Soc.* **1954**, 1291-1297.
21. Francis, A.W. "The Active Agent in Aqueous Bromination" *J. Am. Chem. Soc.* **1925**, *47*, 2340-2348.

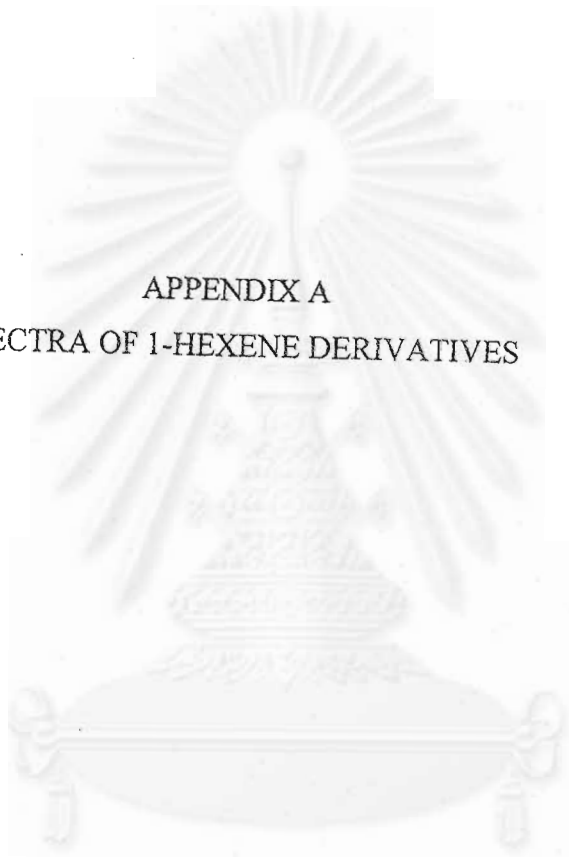


**APPENDICES**

จุฬาลงกรณ์มหาวิทยาลัย



APPENDIX A  
SPECTRA OF 1-HEXENE DERIVATIVES



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

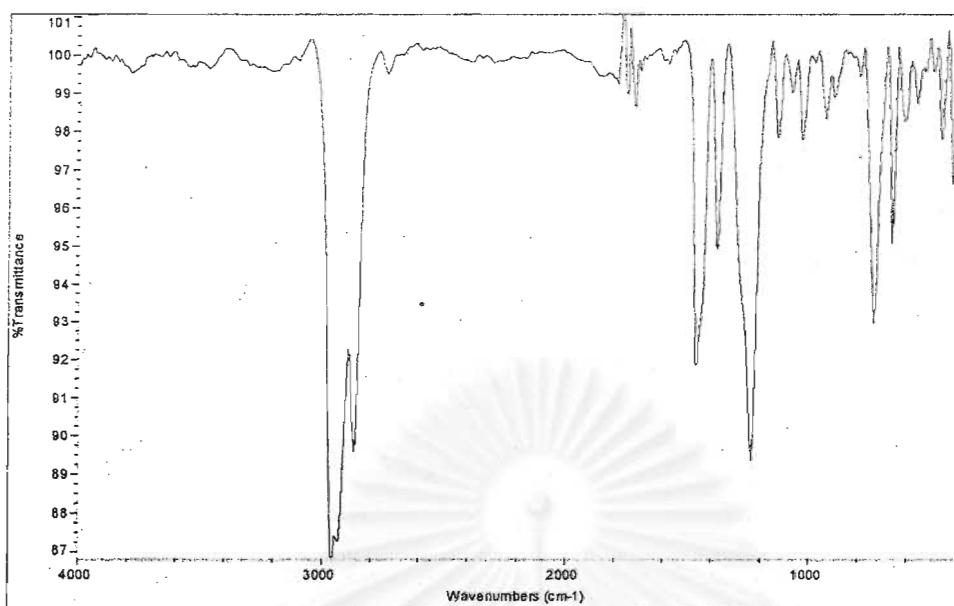


Figure A1 The FTIR spectrum of mixture 1H

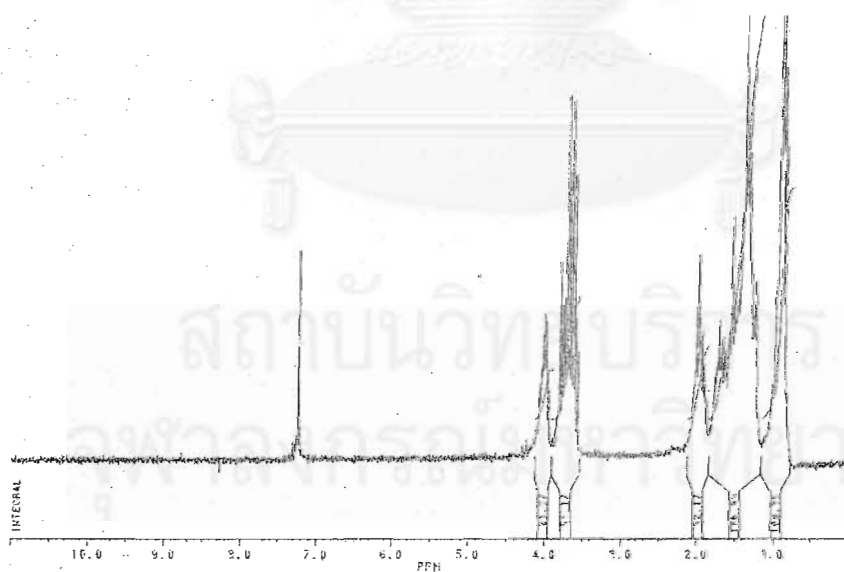


Figure A2 The <sup>1</sup>H-NMR spectrum of mixture 1H

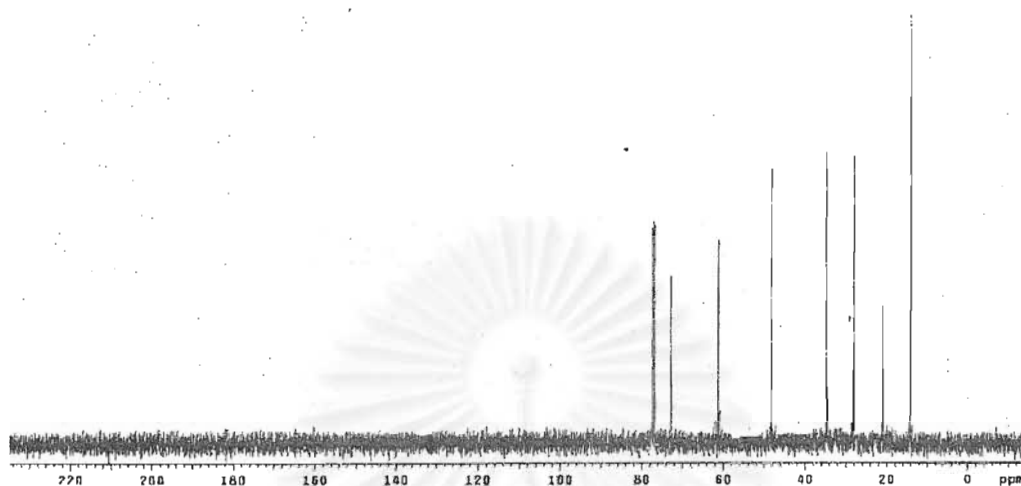


Figure A3 The  $^{13}\text{C}$ -NMR spectrum of mixture 1H

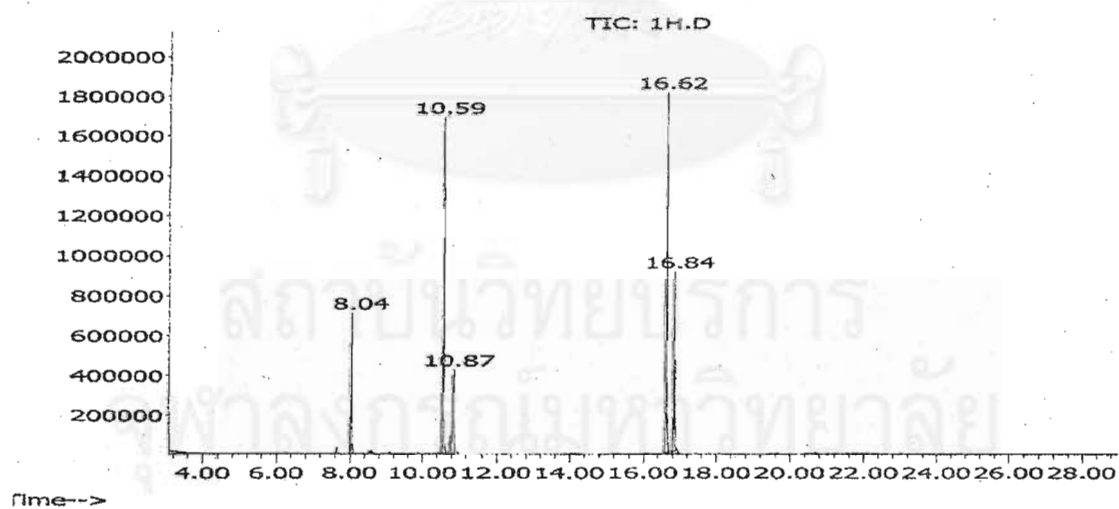


Figure A4 The gas chromatogram of mixture 1H

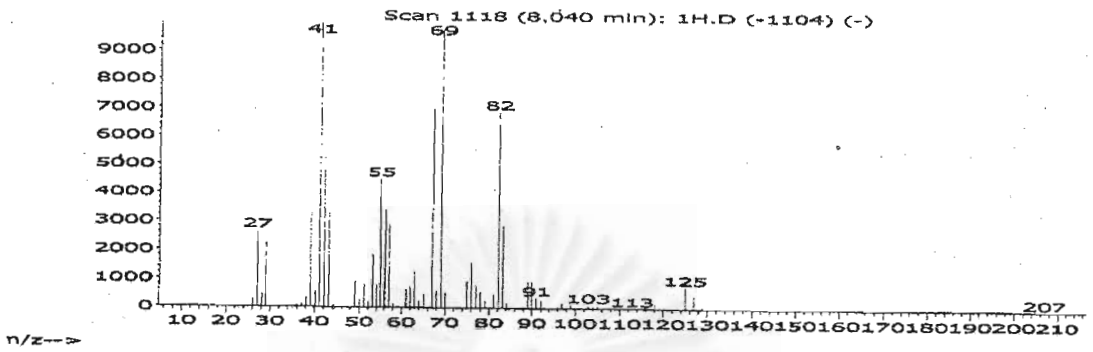


Figure A5 The mass spectrum of mixture 1H at  $t_R = 8.04$  min

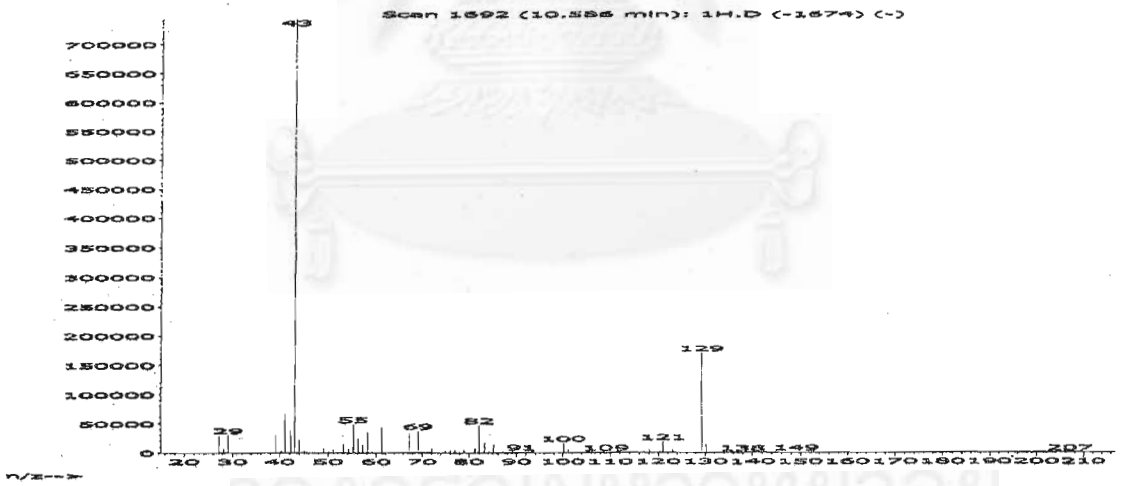


Figure A6 The mass spectrum of mixture 1H at  $t_R = 10.58$  min

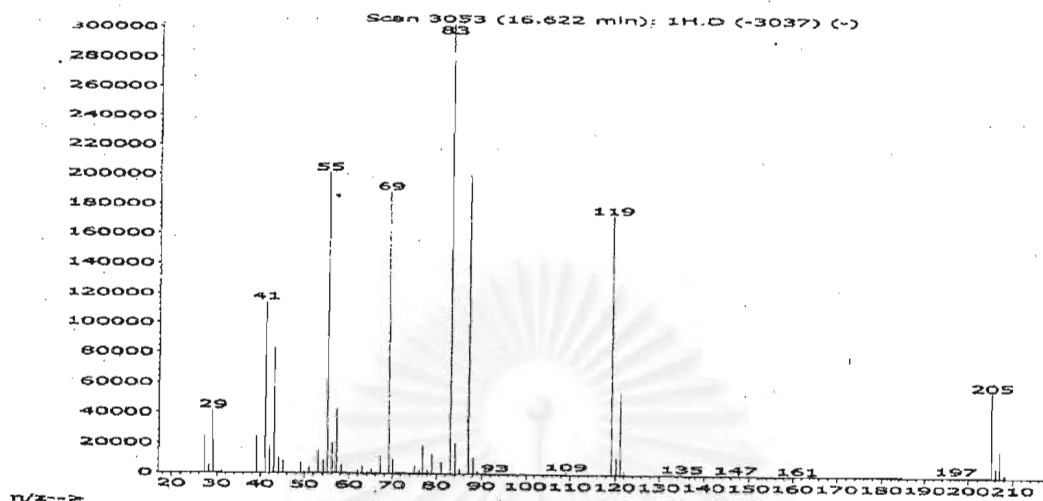


Figure A7 The mass spectrum of mixture 1H at  $t_R = 16.62$  min

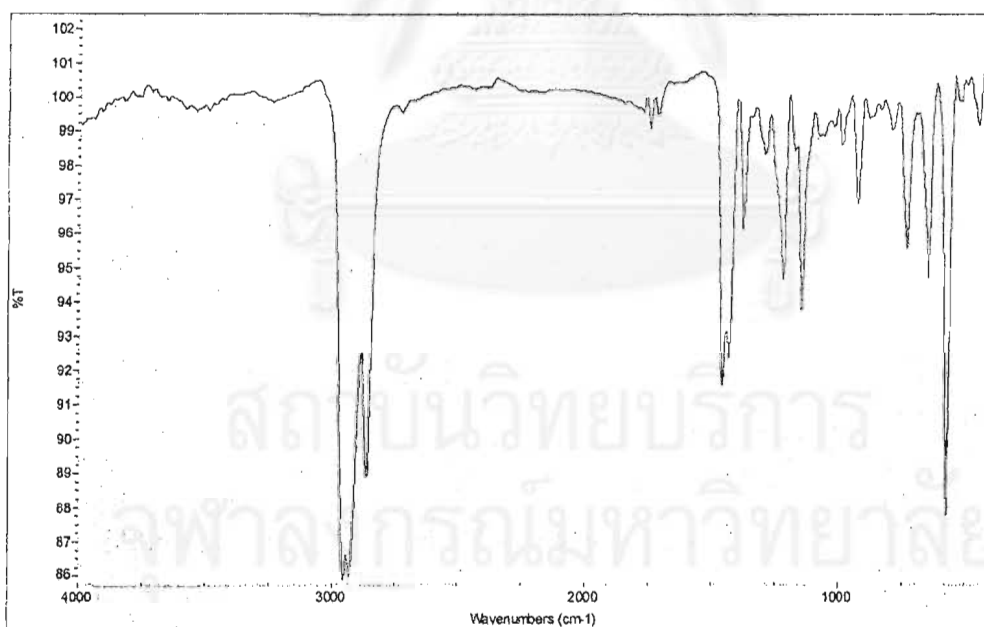


Figure A8 The FTIR spectrum of mixture 2H

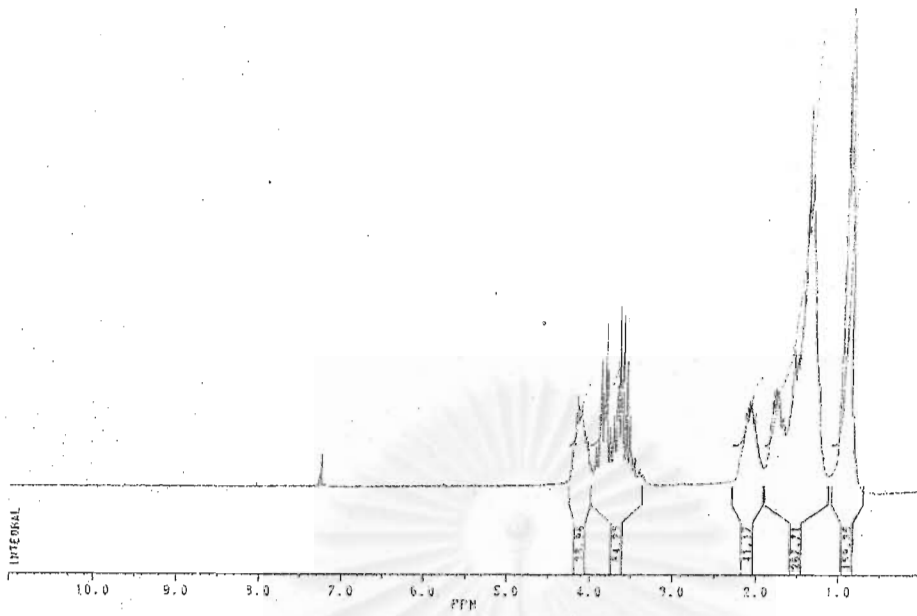


Figure A9 The  $^1\text{H-NMR}$  spectrum of mixture 2H

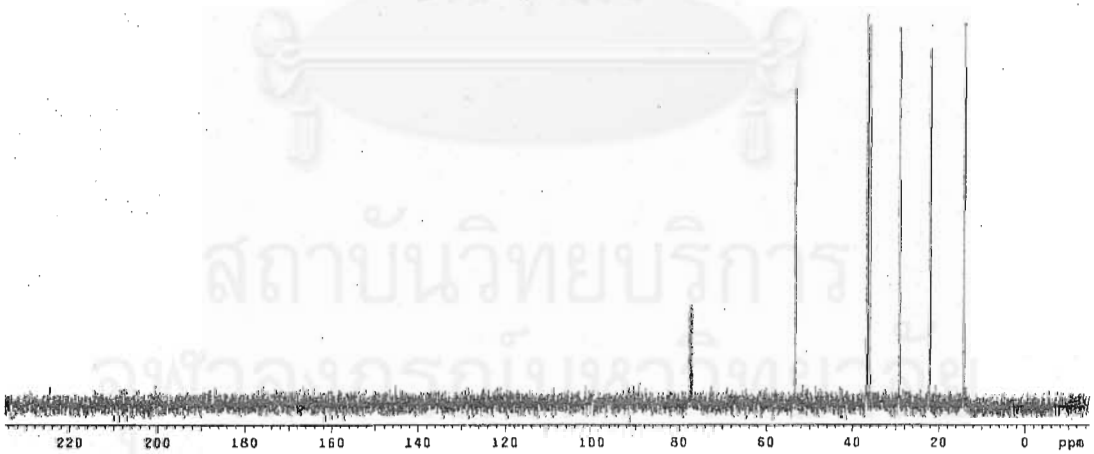


Figure A10 The  $^{13}\text{C-NMR}$  spectrum of mixture 2H

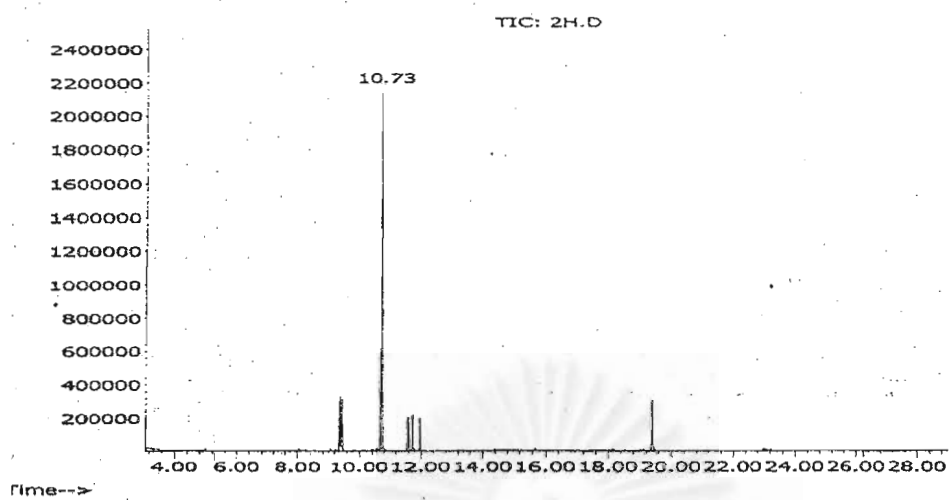


Figure A11 The gas chromatogram of mixture 2H

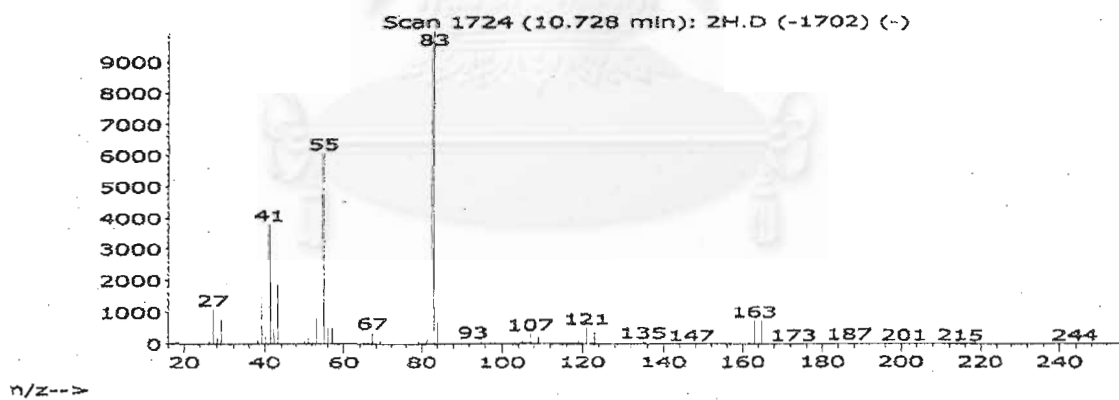


Figure A12 The mass spectrum of mixture 2H at  $t_R = 10.73$  min

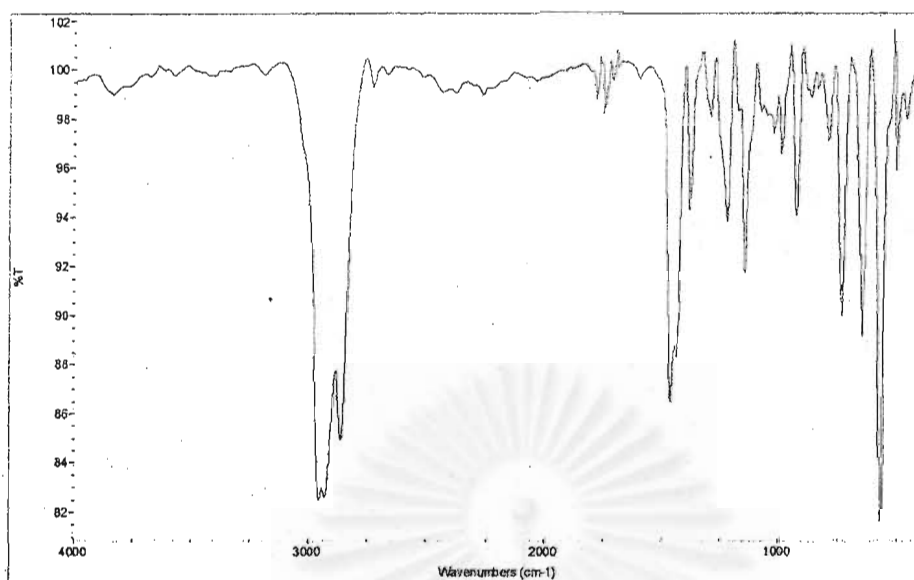


Figure A13 The FTIR spectrum of mixture 3H

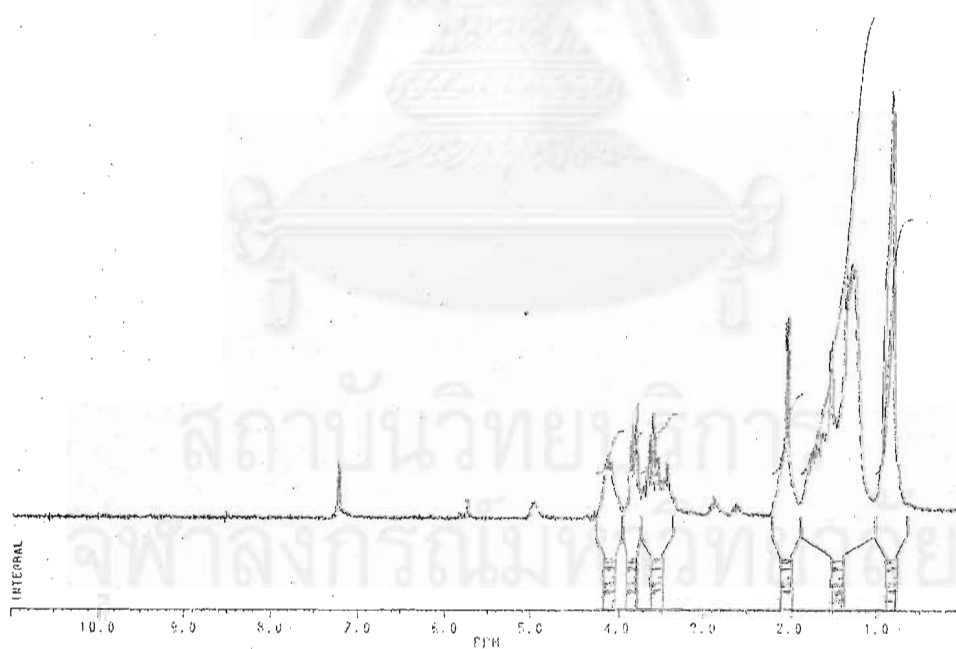


Figure A14 The <sup>1</sup>H-NMR spectrum of mixture 3H



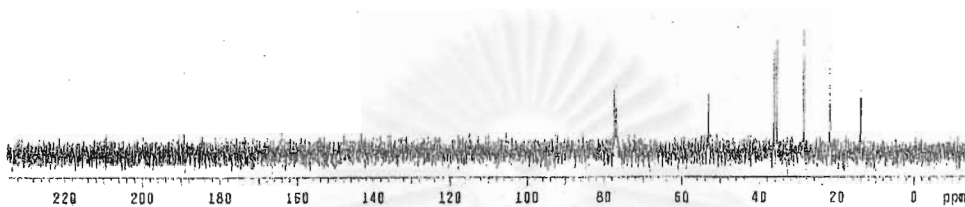


Figure A15 The  $^{13}\text{C}$ -NMR spectrum of mixture 3H

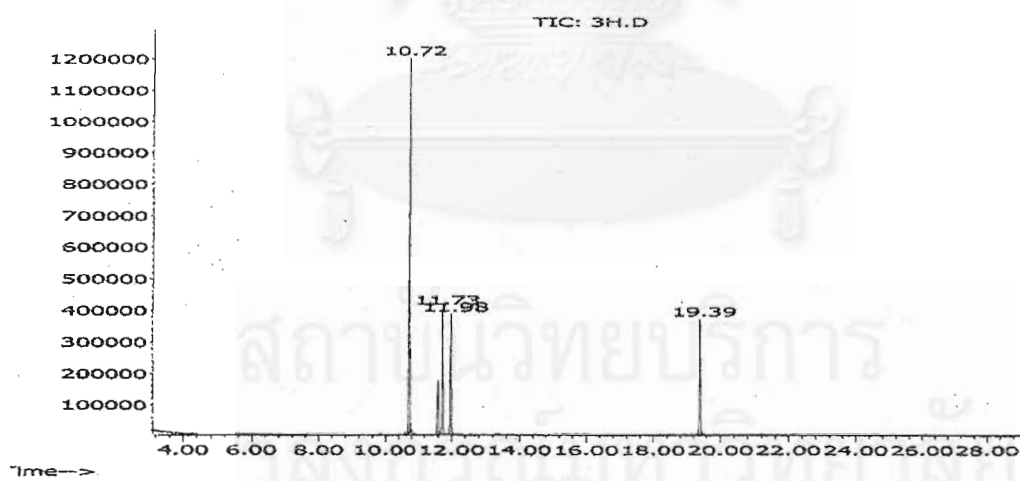


Figure A16 The gas chromatogram of mixture 3H

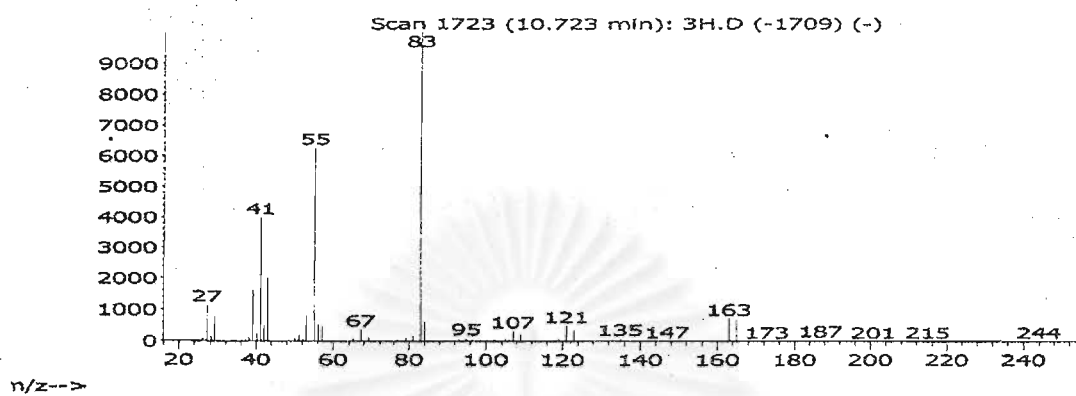


Figure A17 The mass spectrum of mixture 3H at  $t_R = 10.72$  min

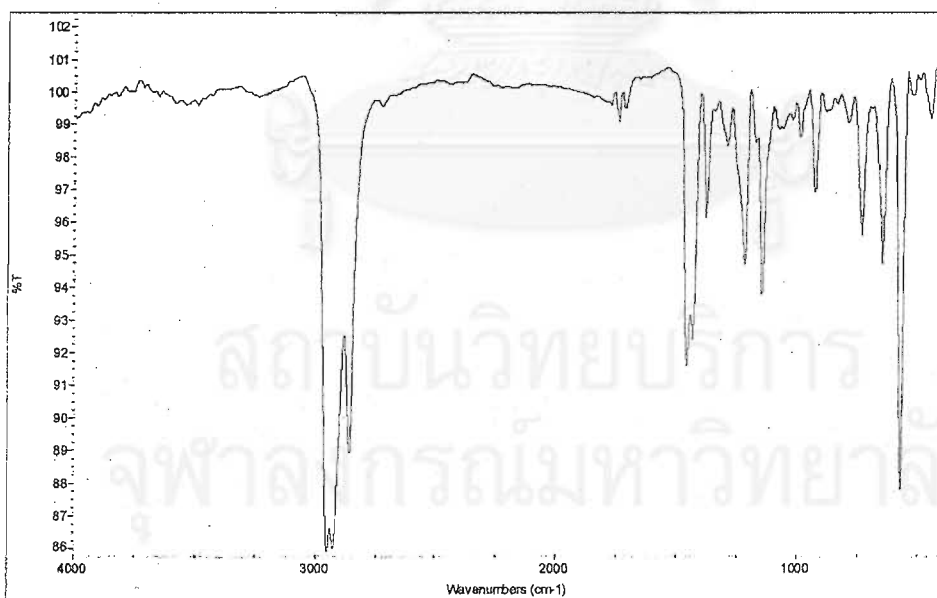


Figure A18 The FTIR spectrum of mixture 4H

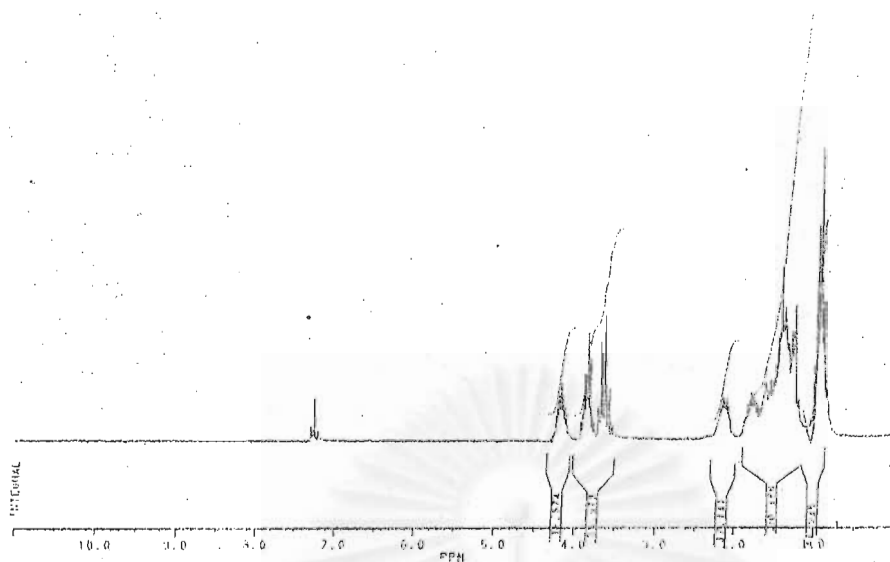


Figure A19 The  $^1\text{H-NMR}$  spectrum of mixture 4H

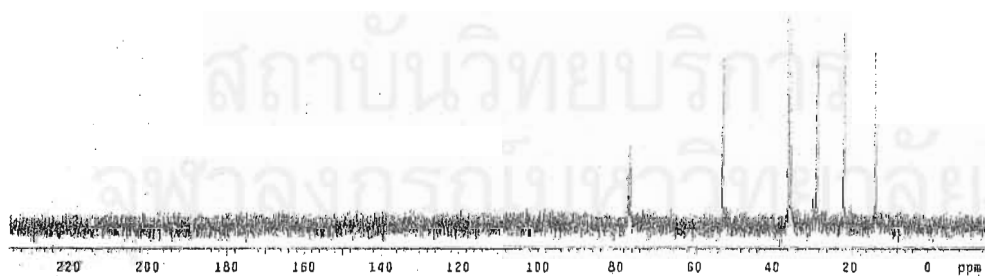


Figure A20 The  $^{13}\text{C-NMR}$  spectrum of mixture 4H

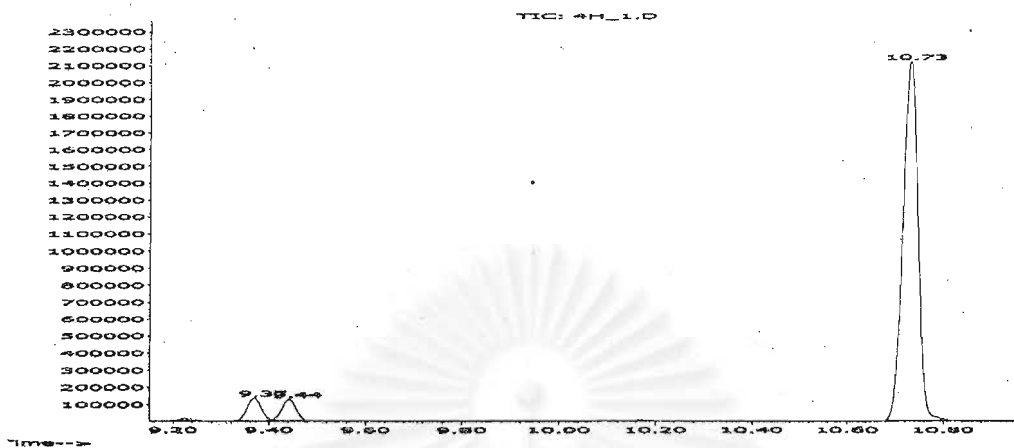


Figure A21 The gas chromatogram of mixture 4H

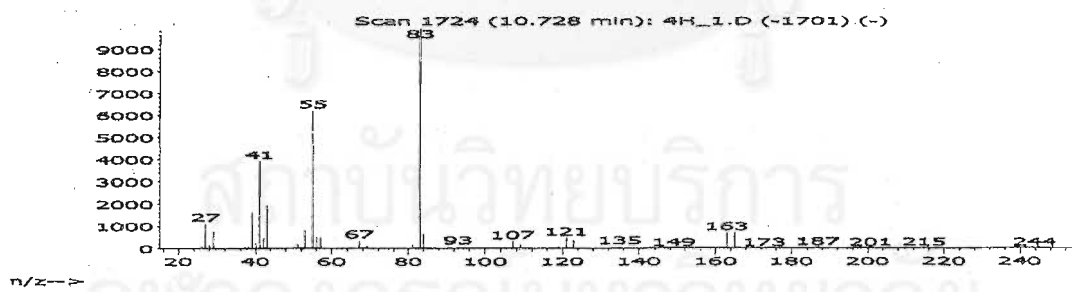


Figure A22 The mass spectrum of mixture 4H at  $t_R = 10.72$  min

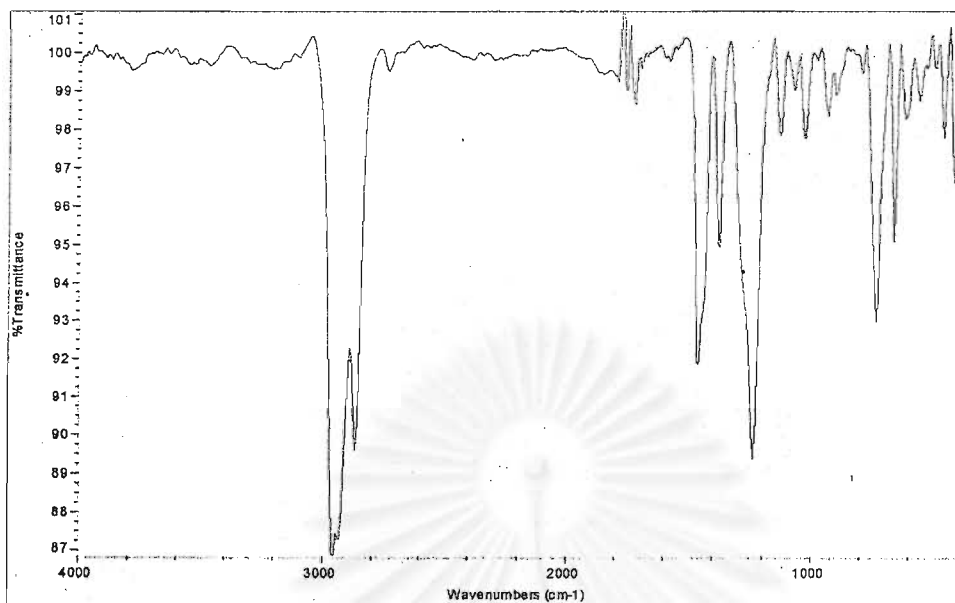


Figure A23 The FTIR spectrum of mixture 5H



Figure A24 The <sup>1</sup>H-NMR spectrum of mixture 5H

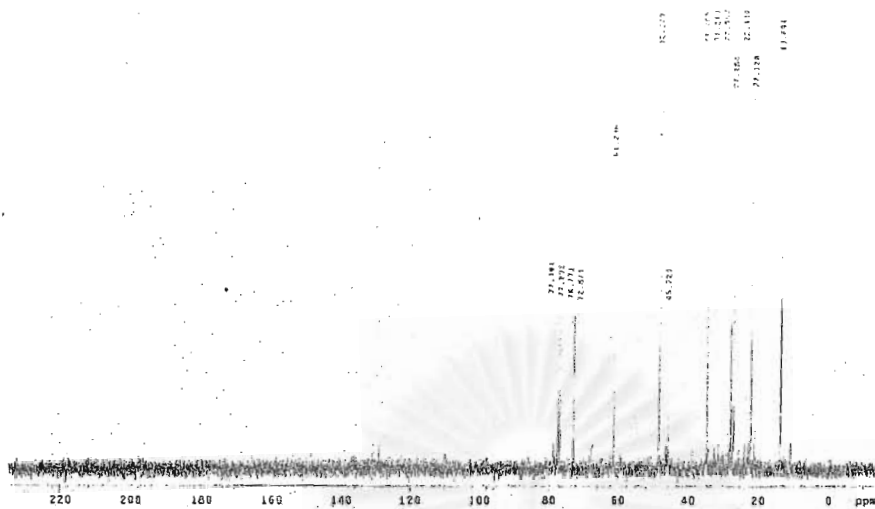


Figure A25 The  $^{13}\text{C}$ -NMR spectrum of mixture 5H

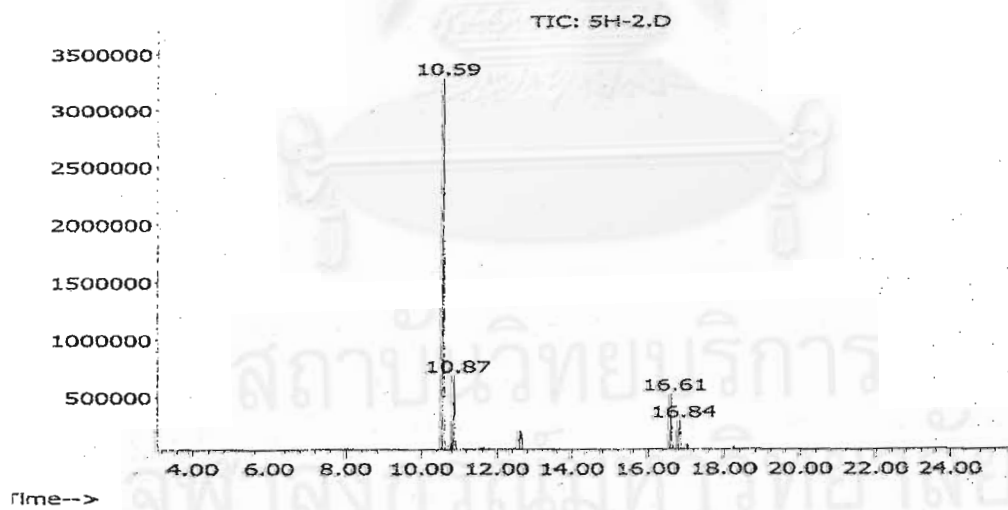


Figure A26 The gas chromatogram of mixture 5H

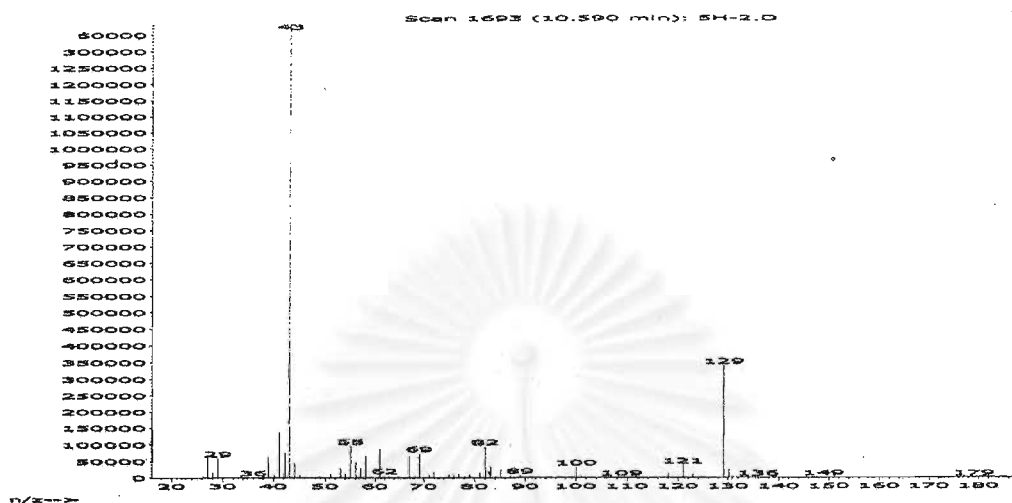


Figure A27 The mass spectrum of mixture 5H at  $t_R = 10.59$  min

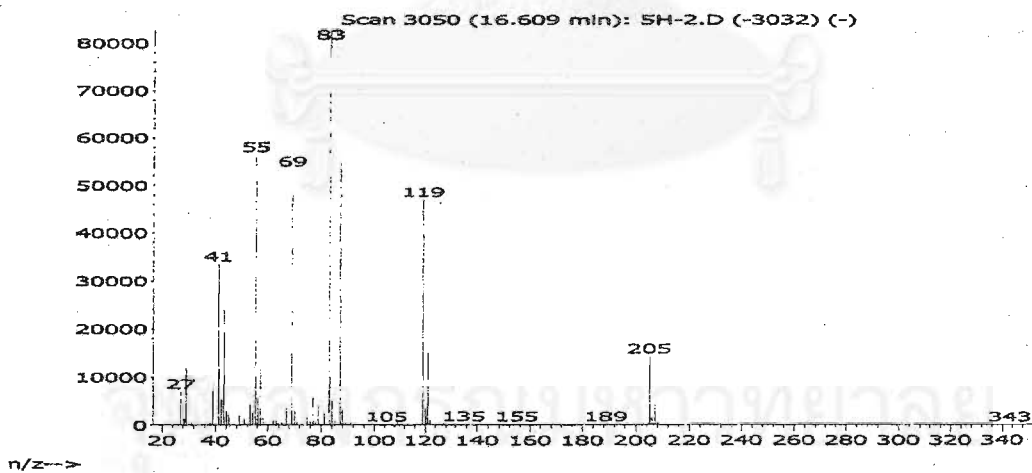


Figure A28 The mass spectrum of mixture 5H at  $t_R = 16.61$  min

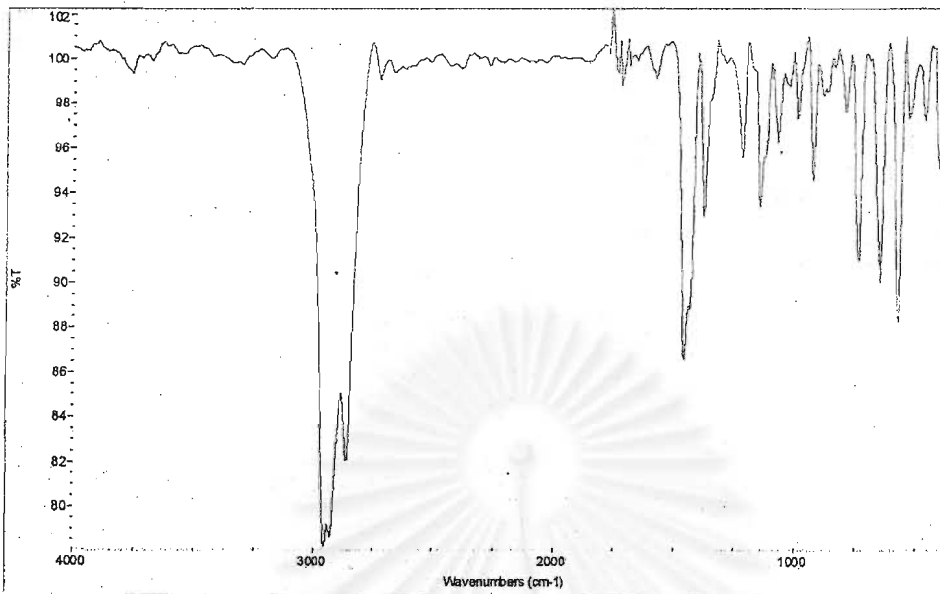


Figure A29 The FTIR spectrum of mixture 6H



Figure A30 The <sup>1</sup>H-NMR spectrum of mixture 6H



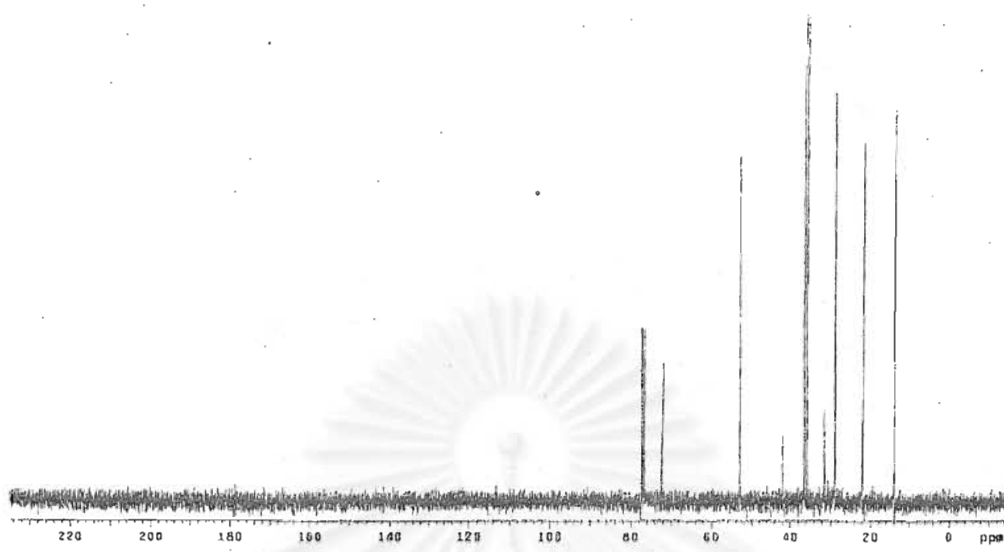


Figure A31 The  $^{13}\text{C}$ -NMR spectrum of mixture 6H

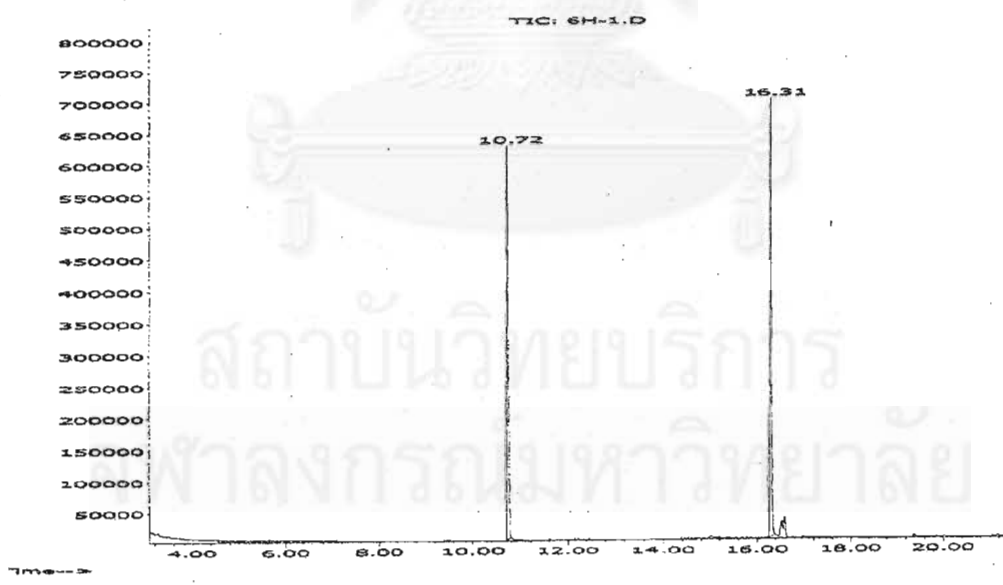


Figure A32 The gas chromatogram of mixture 6H

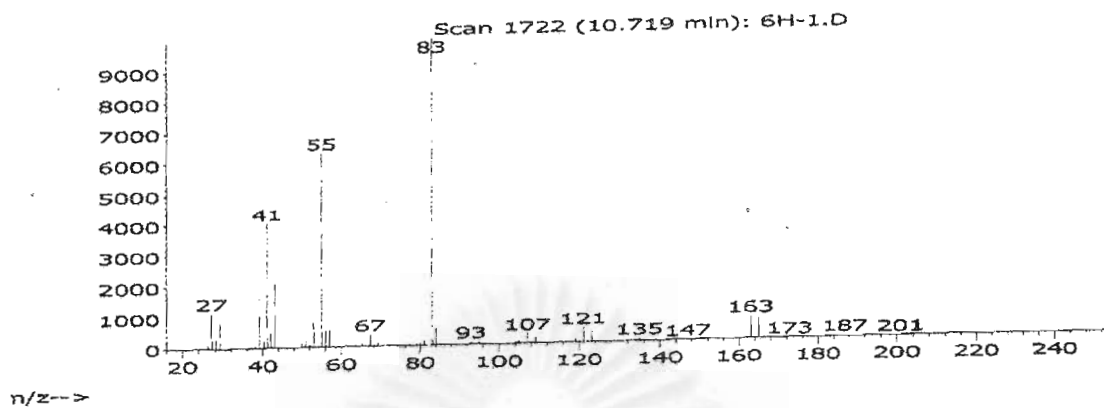


Figure A33 The mass spectrum of mixture 6H at  $t_R = 10.72$  min



Figure A34 The mass spectrum of mixture 6H at  $t_R = 16.30$  min

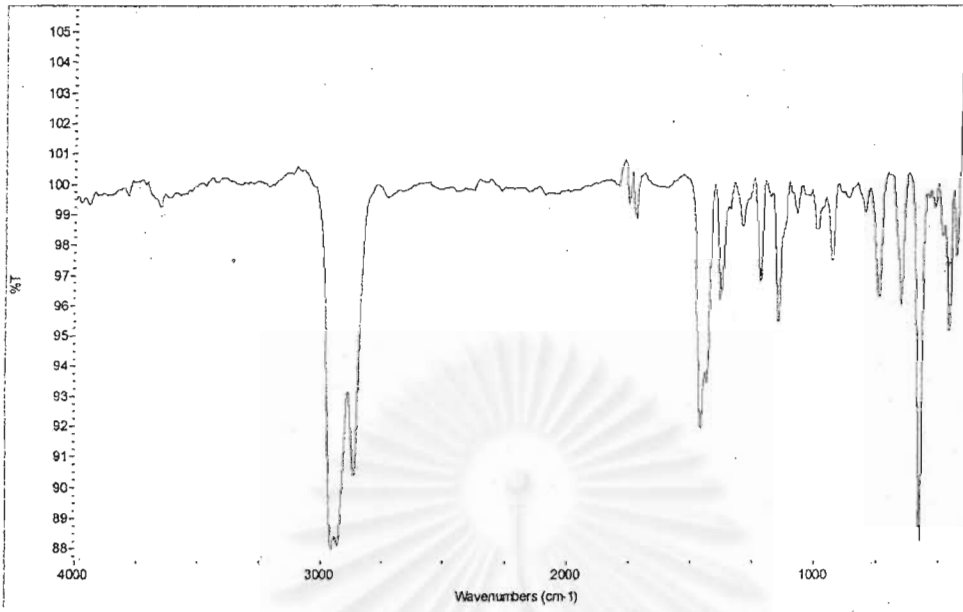


Figure A35 The FTIR spectrum of mixture 7H

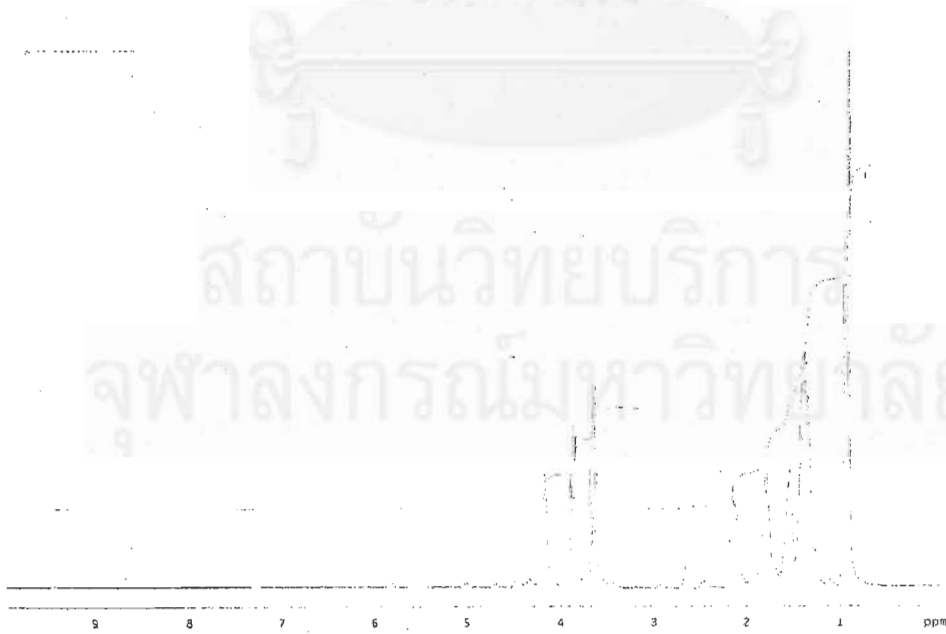


Figure A36 The <sup>1</sup>H-NMR spectrum of mixture 7H

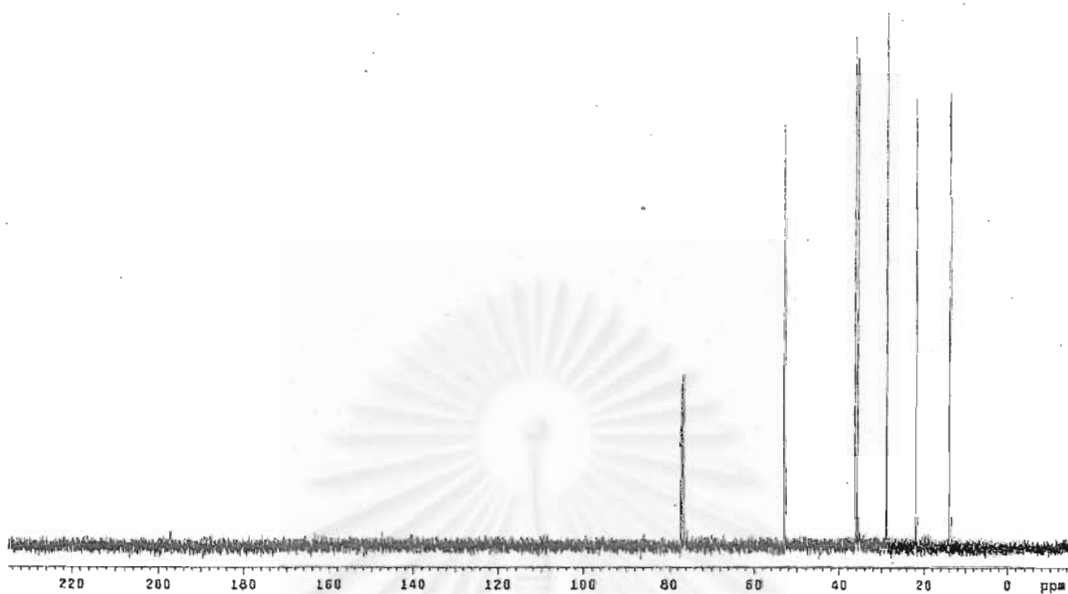


Figure A37 The  $^{13}\text{C}$ -NMR spectrum of mixture 7H

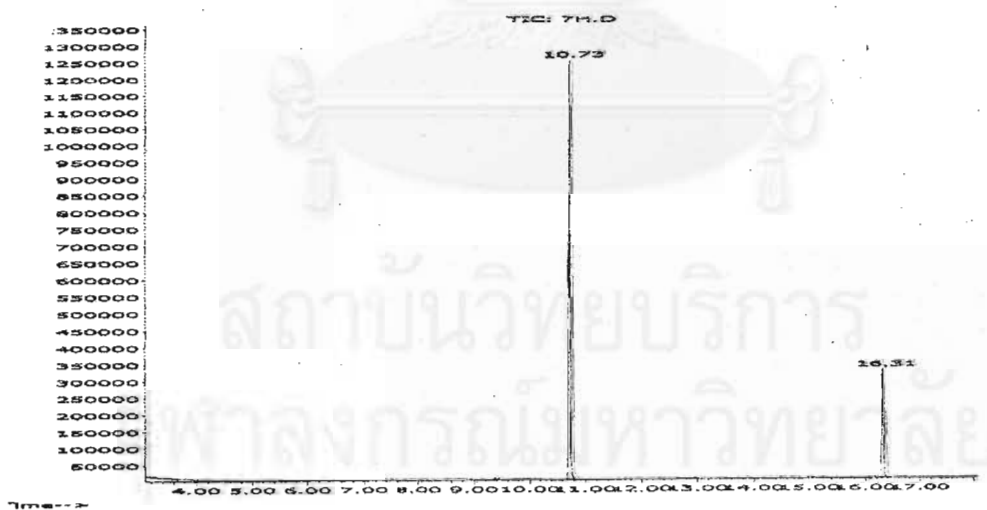


Figure A38 The gas chromatogram of mixture 7H

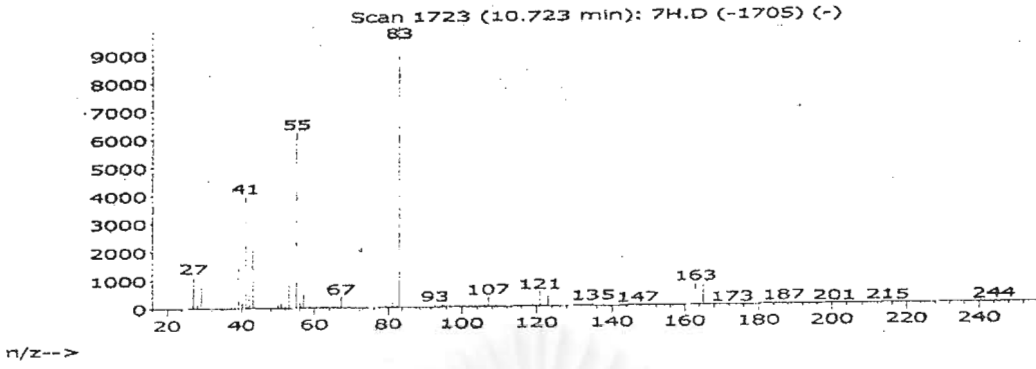


Figure A39 The mass spectrum of mixture 7H at  $t_R = 10.73$  min

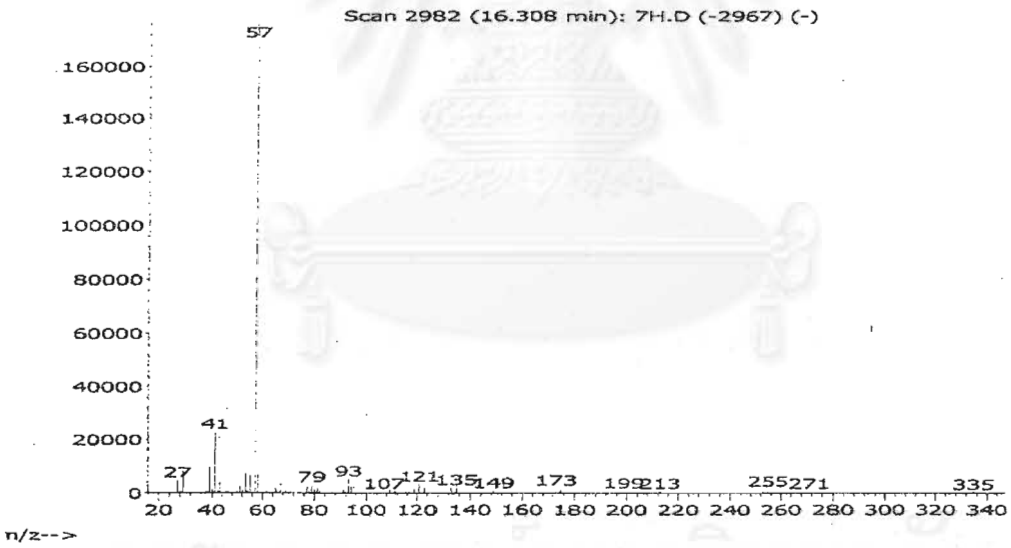


Figure A40 The mass spectrum of mixture 7H at  $t_R = 16.30$  min

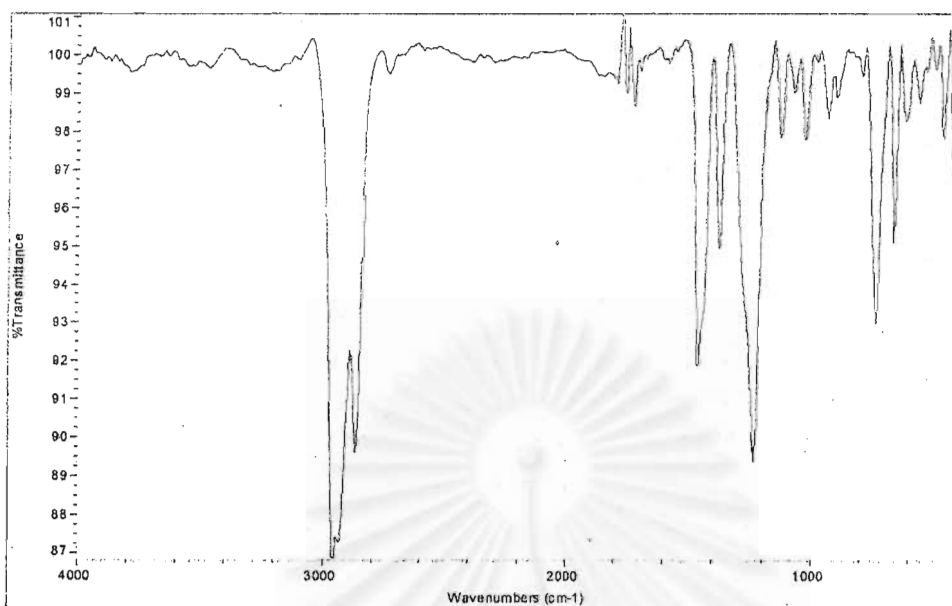


Figure A41 The FTIR spectrum of mixture 8H



Figure A42 The <sup>1</sup>H-NMR spectra of mixture 8H

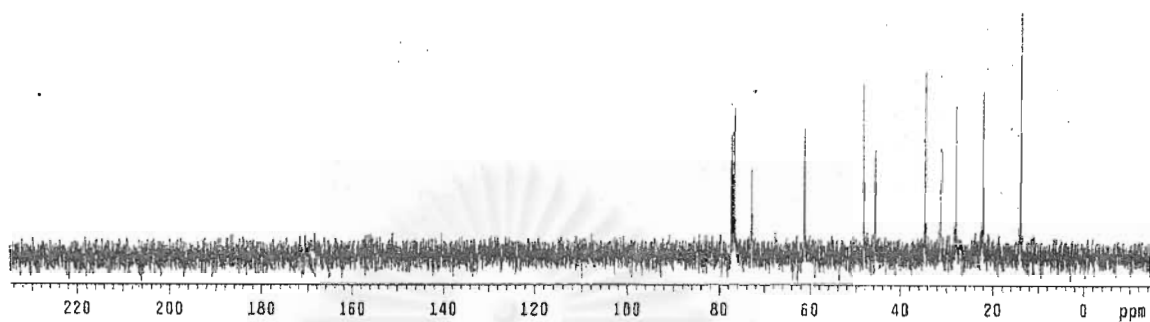


Figure A43 The  $^{13}\text{C}$ -NMR spectra of mixture 8H

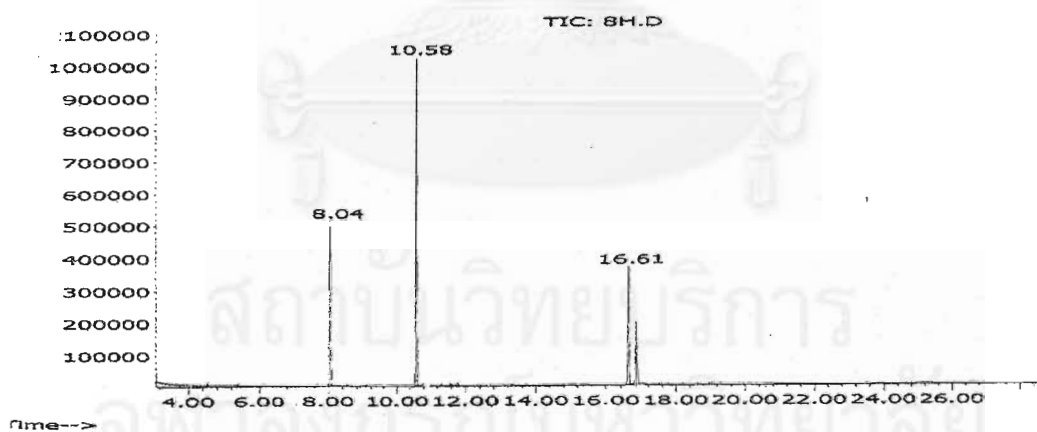


Figure A44 The gas chromatogram of mixture 8H

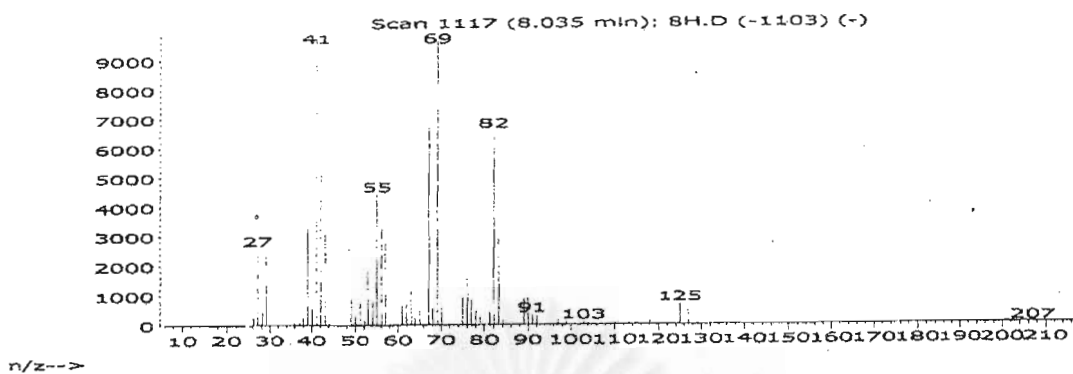


Figure A45 The mass spectrum of mixture 8H at  $t_R = 8.03$  min

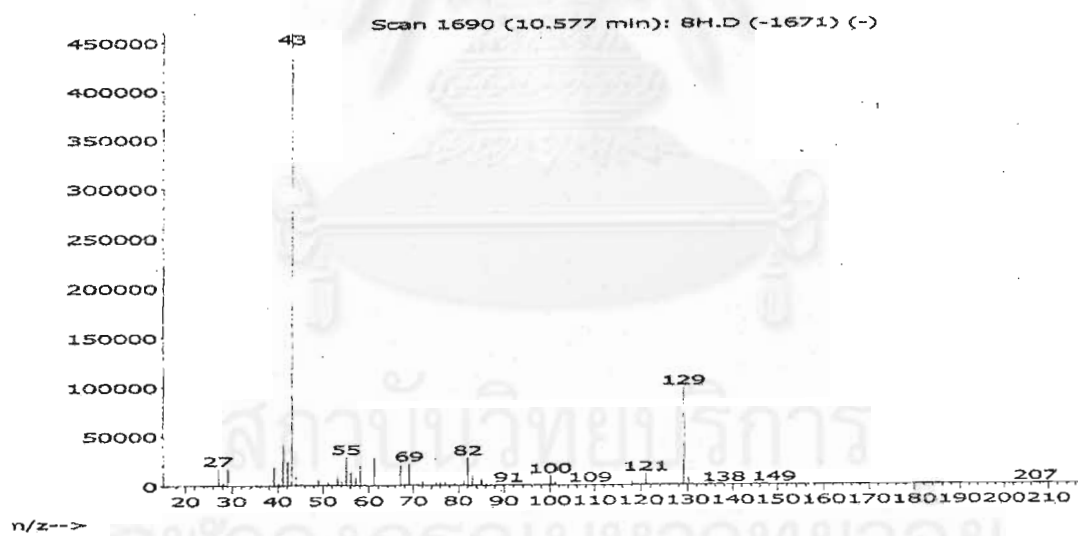


Figure A46 The mass spectrum of mixture 8H at  $t_R = 10.57$  min



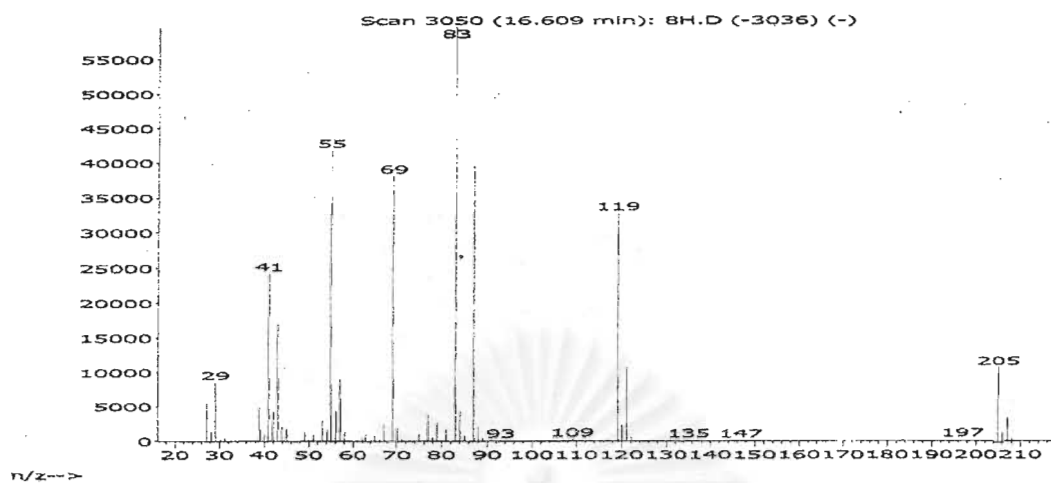


Figure A47 The mass spectrum of mixture 8H at  $t_R = 16.60$  min

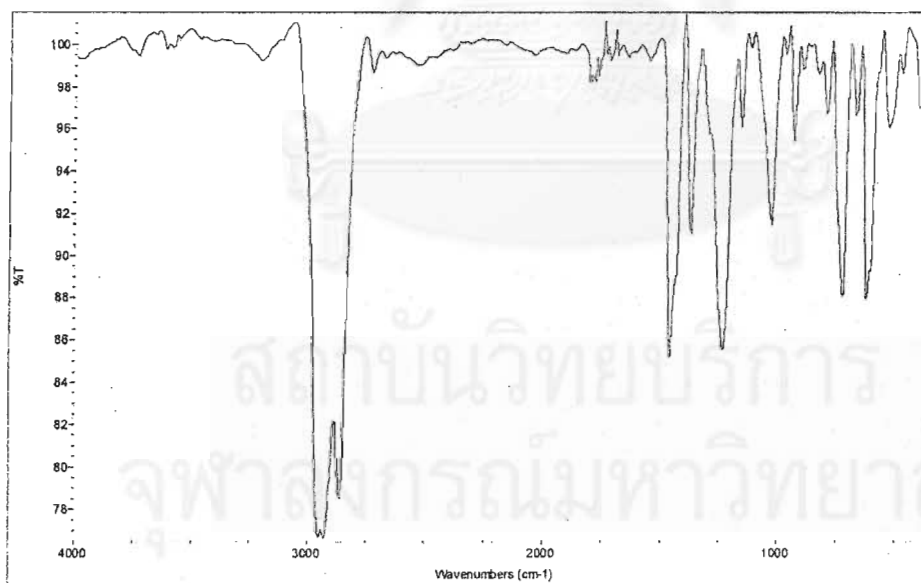


Figure A48 The FTIR spectrum of mixture 9H

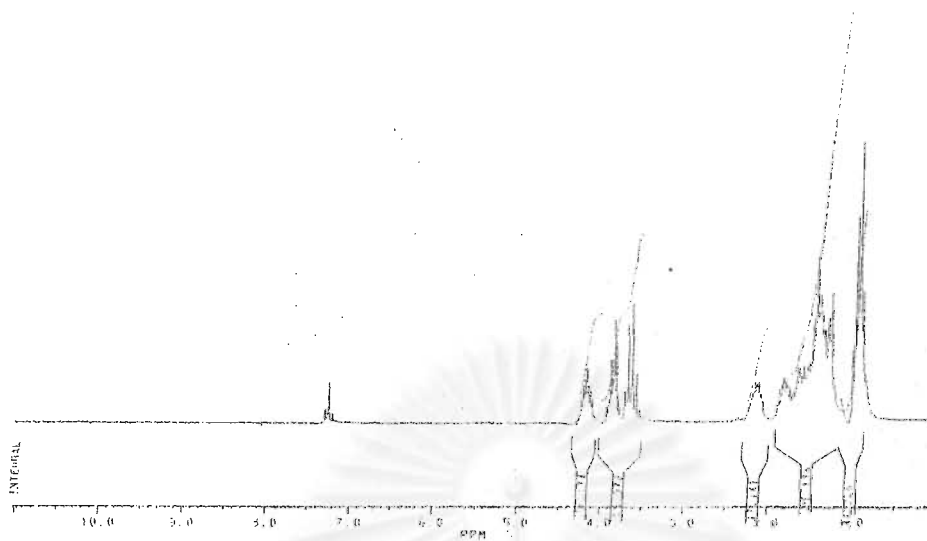


Figure A49 The  $^1\text{H}$ -NMR spectrum of mixture 9H

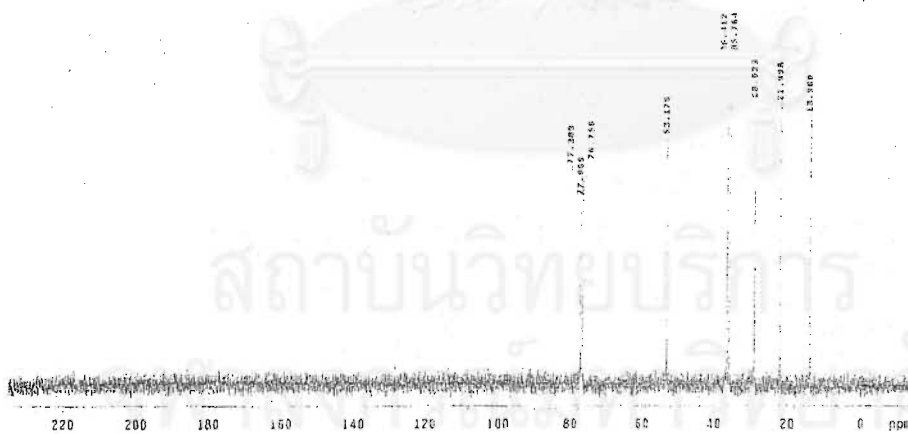


Figure A50 The  $^{13}\text{C}$ -NMR spectrum of mixture 9H

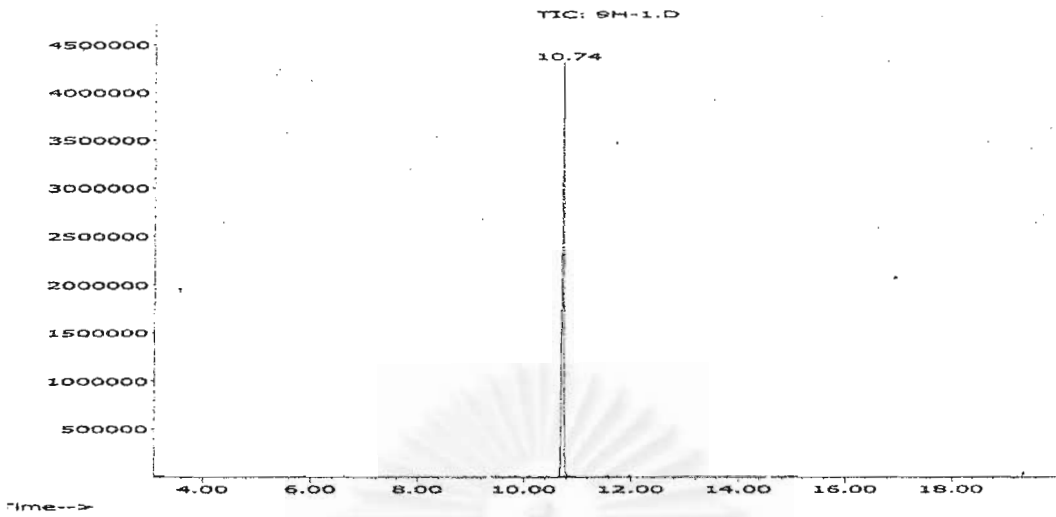


Figure A51 The gas chromatogram of mixture 9H

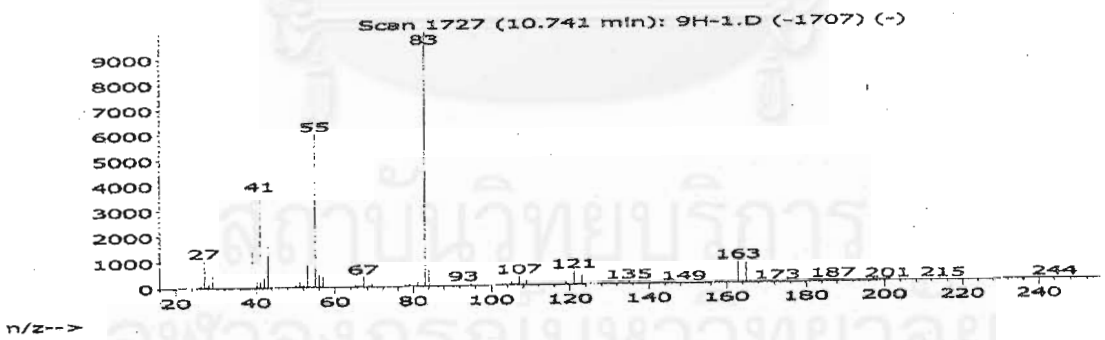


Figure A52 The mass spectrum of mixture 9H at  $t_R = 10.74$  min

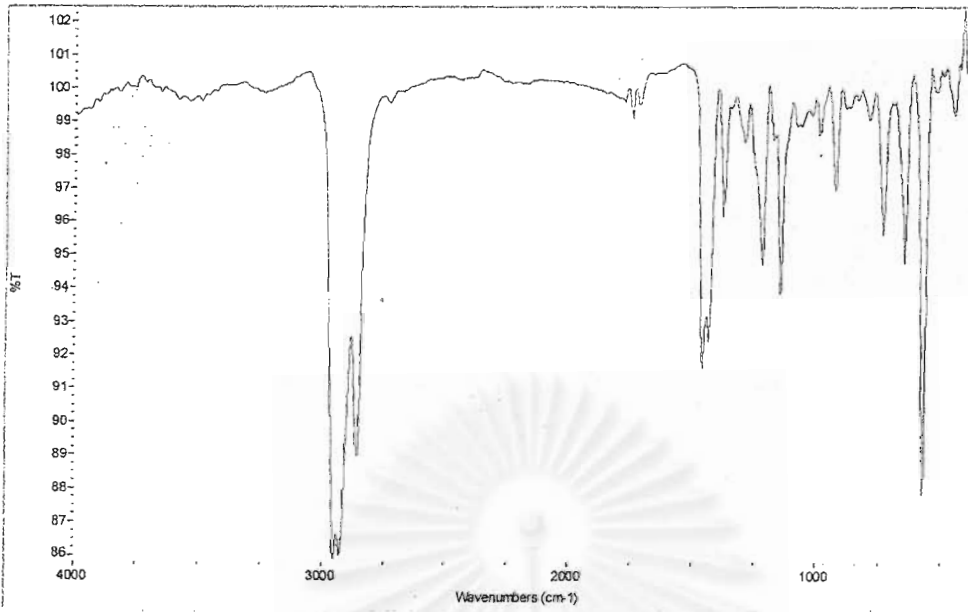


Figure A53 The FTIR spectrum of mixture 10H

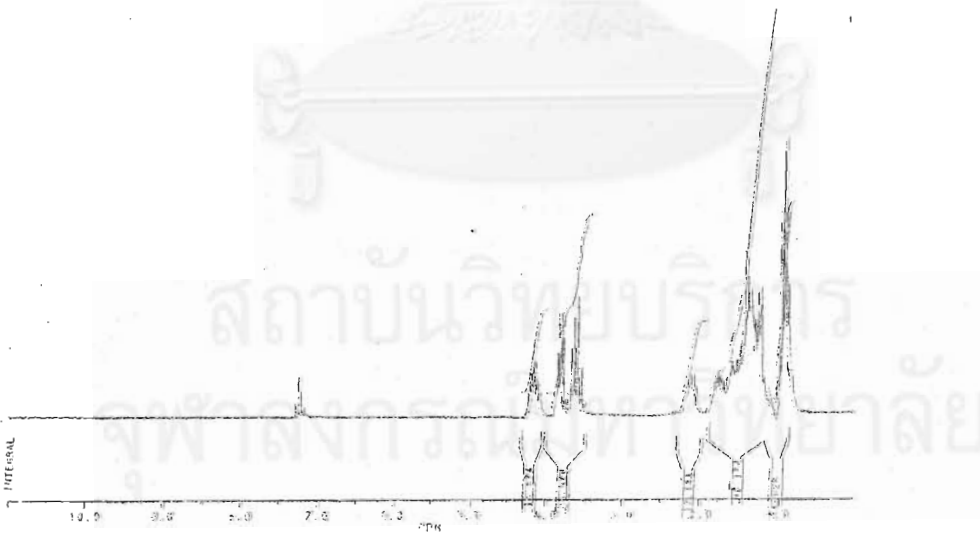


Figure A54 The <sup>1</sup>H-NMR spectrum of mixture 10H

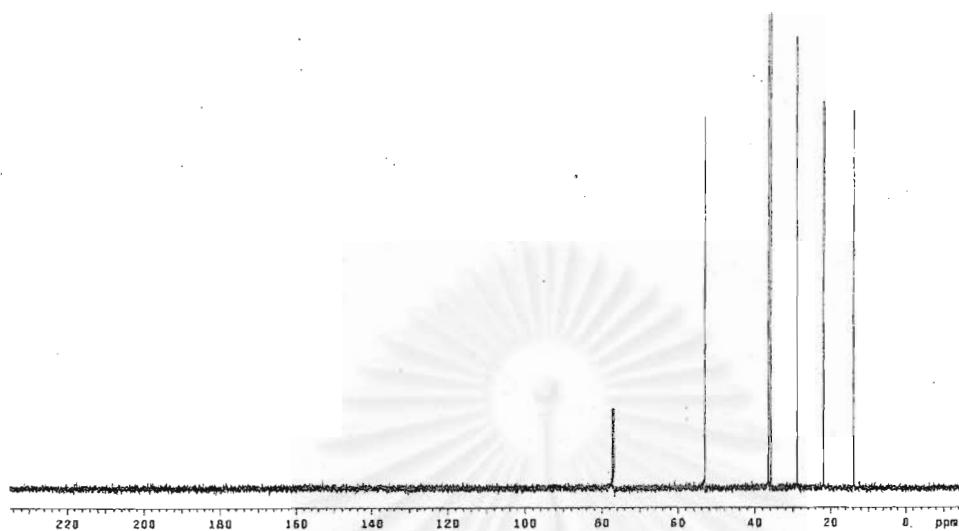


Figure A55 The  $^{13}\text{C}$ -NMR spectrum of mixture 10H

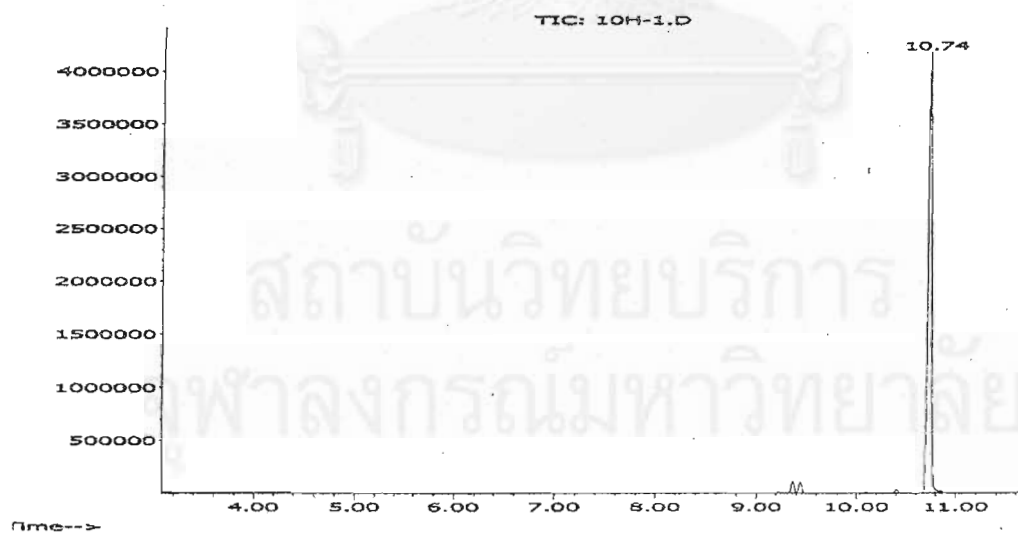


Figure A56 The gas chromatogram of mixture 10H

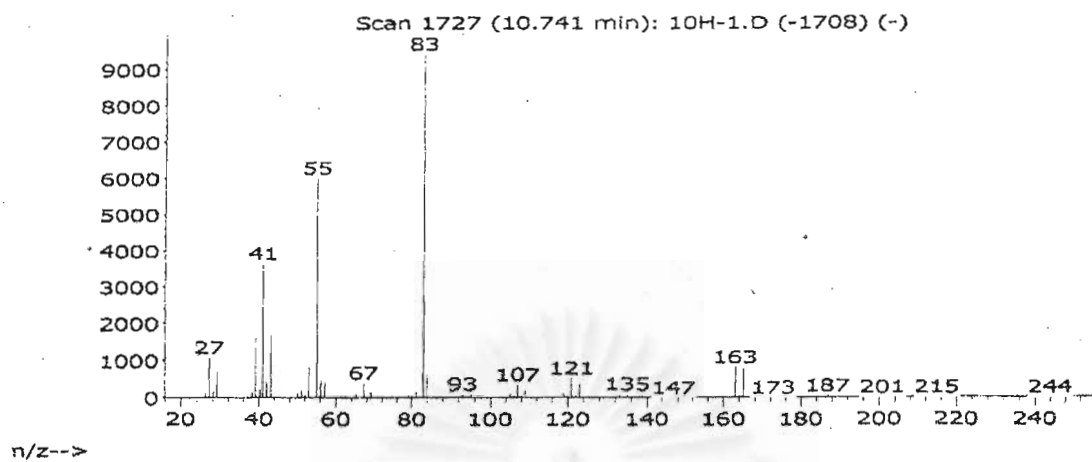
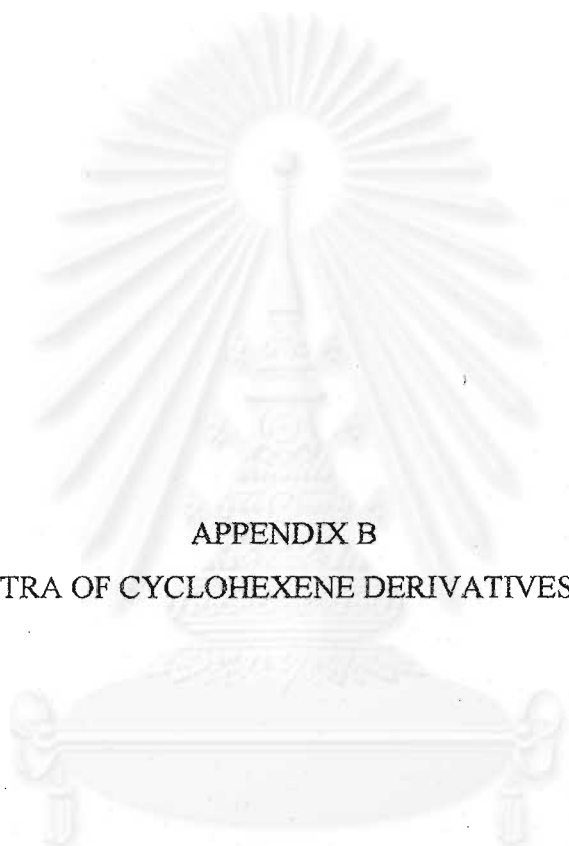


Figure A57 The mass spectrum of mixture 10H at  $t_R = 10.74$  min

จุฬาลงกรณ์มหาวิทยาลัย



APPENDIX B  
SPECTRA OF CYCLOHEXENE DERIVATIVES

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

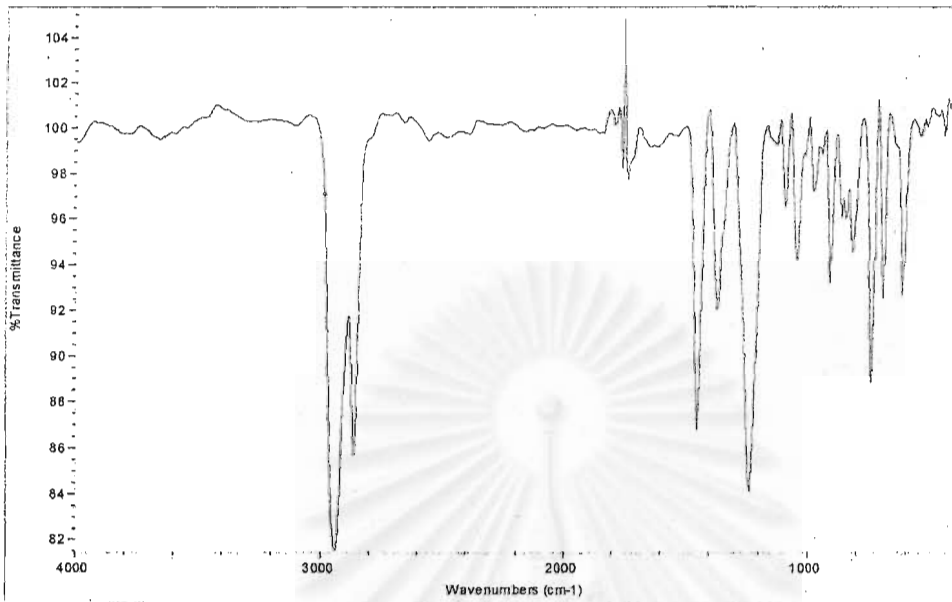


Figure B1 The FTIR spectrum of mixture 1C

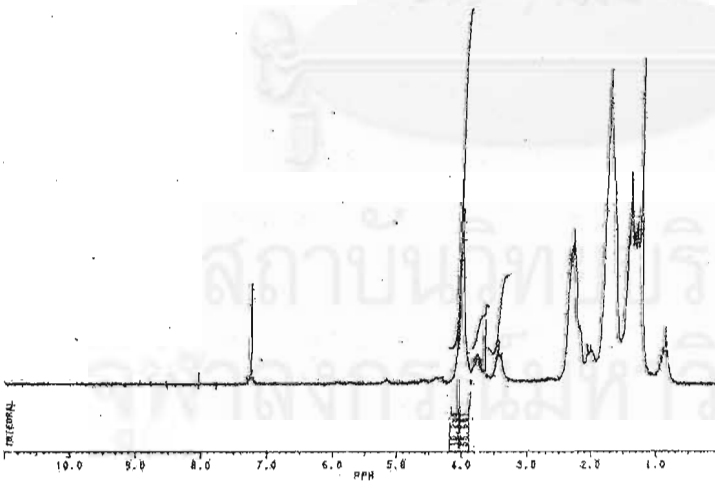


Figure B2 The <sup>1</sup>H-NMR spectrum of mixture 1C



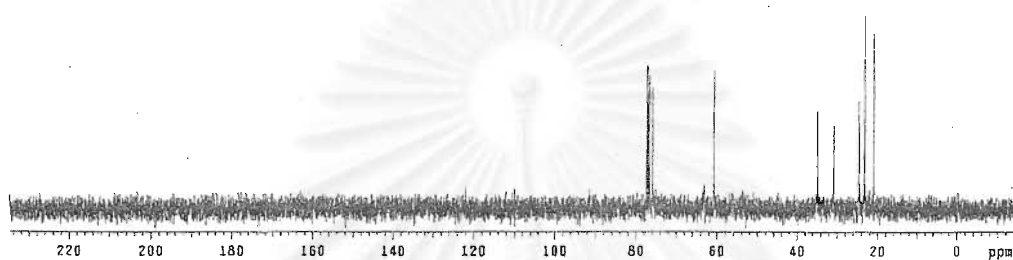


Figure B3 The  $^{13}\text{C}$ -NMR spectrum of mixture 1C

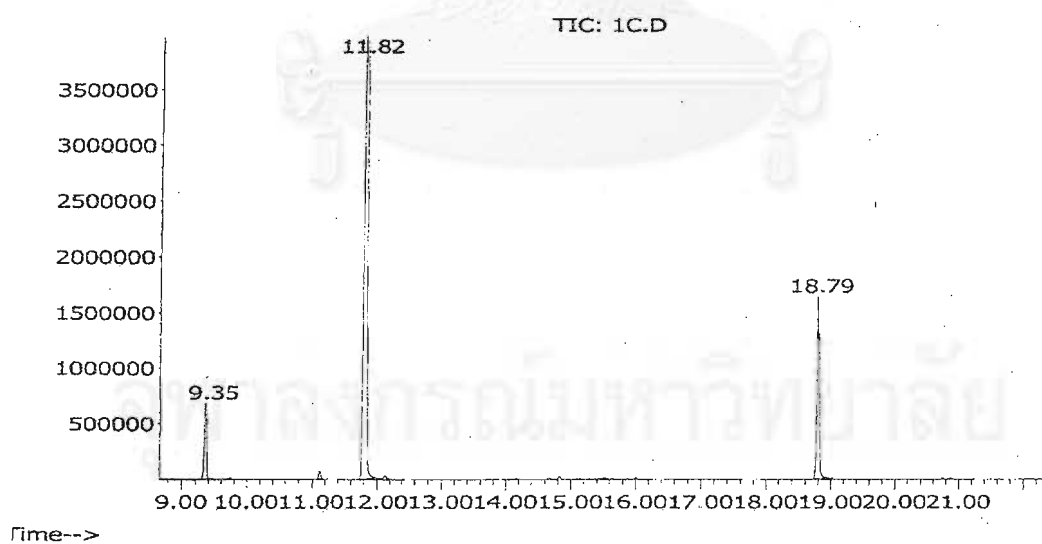


Figure B4 The gas chromatogram of mixture 1C

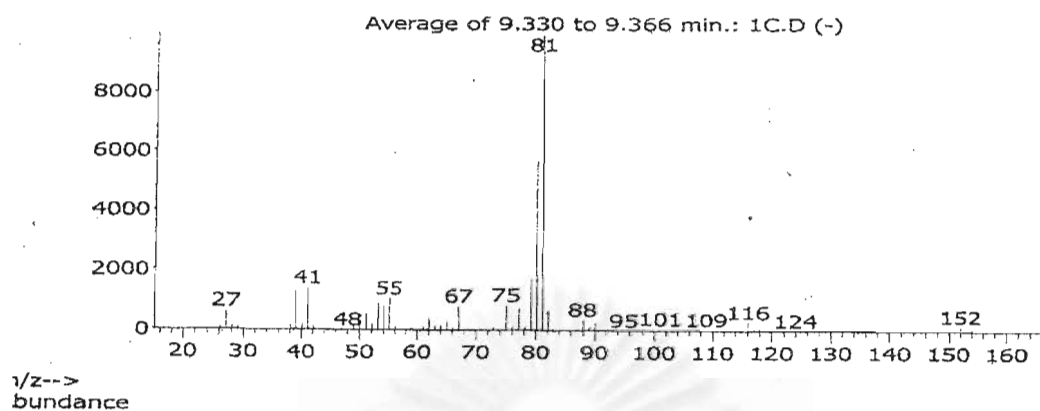


Figure B5 The mass spectrum of mixture 1C at  $t_R = 9.33$  min

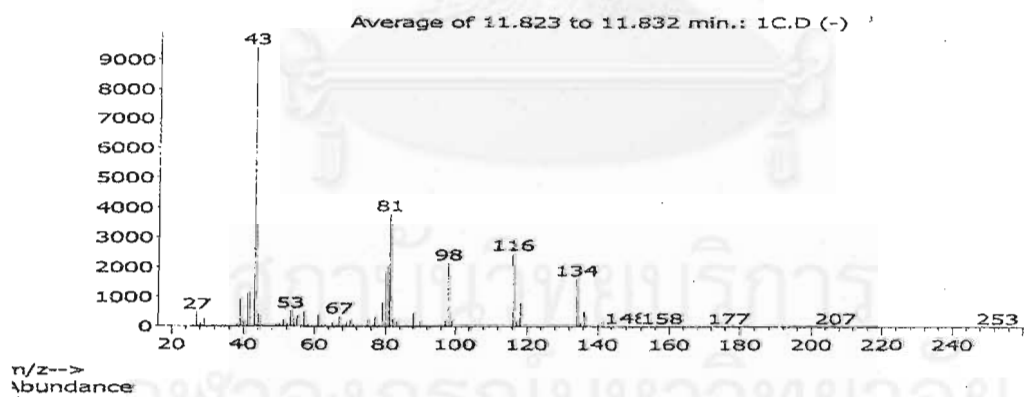


Figure B6 The mass spectrum of mixture 1C at  $t_R = 11.82$  min

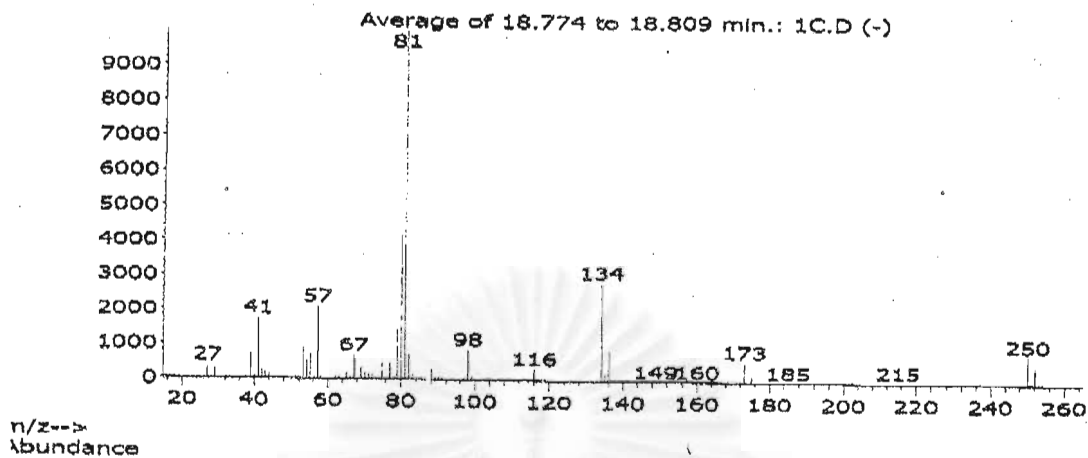


Figure B7 The mass spectrum of mixture 1C at  $t_R = 18.77$  min

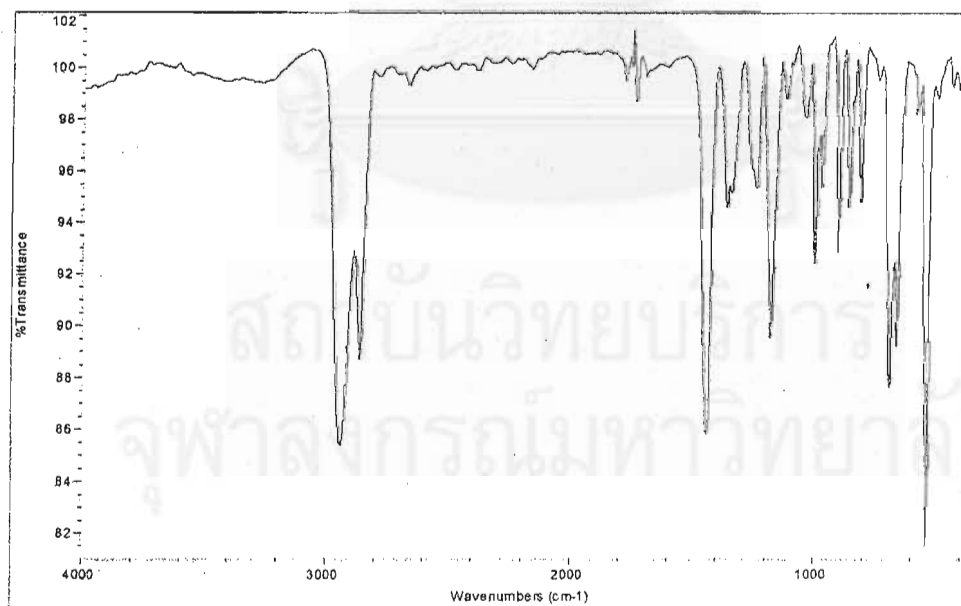


Figure B8 The FTIR spectrum of mixture 2C

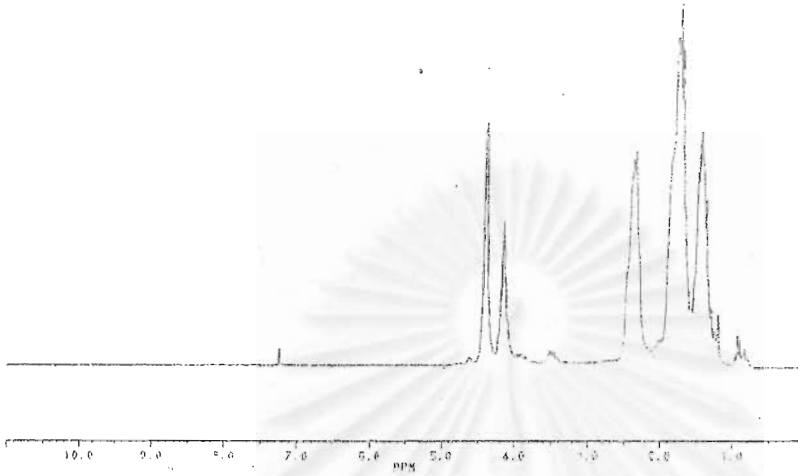


Figure B9 The  $^1\text{H}$ -NMR spectrum of mixture 2C

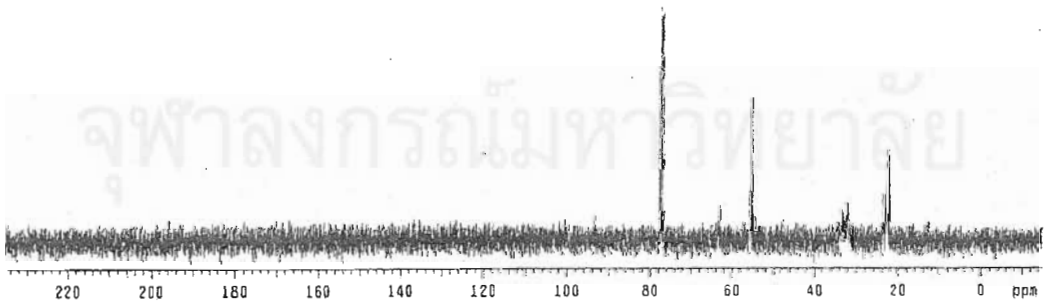


Figure B10 The  $^{13}\text{C}$ -NMR spectrum of mixture 2C

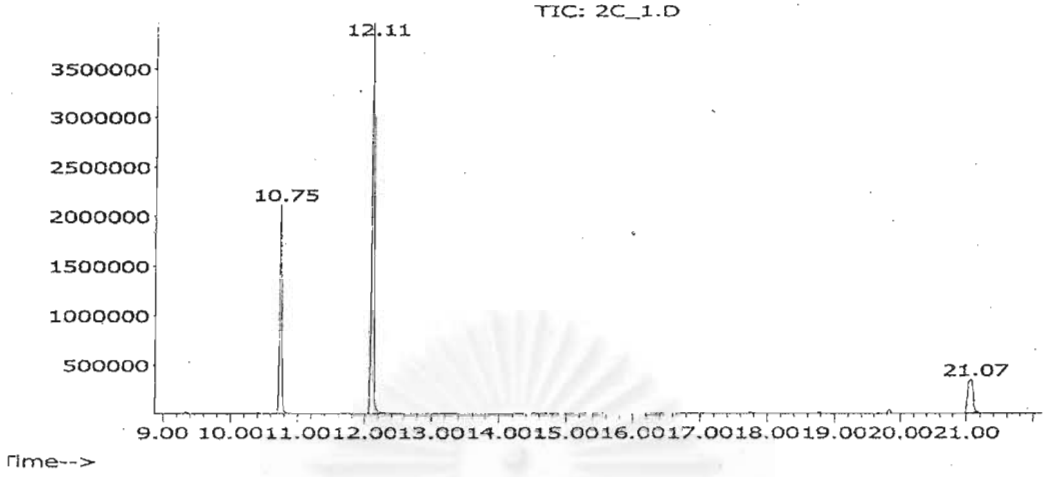


Figure B11 The gas chromatogram of mixture 2C

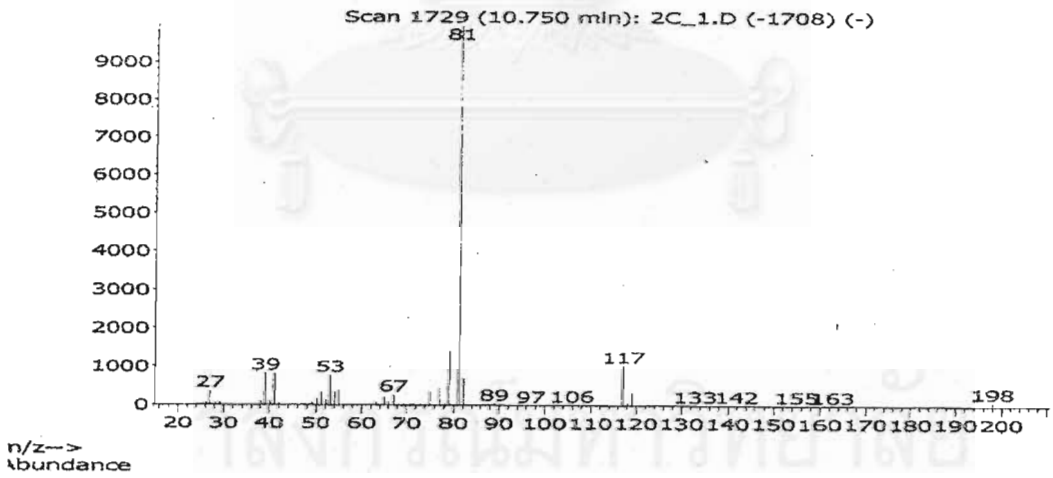


Figure B12 The mass spectrum of mixture 2C at  $t_R = 10.75$  min

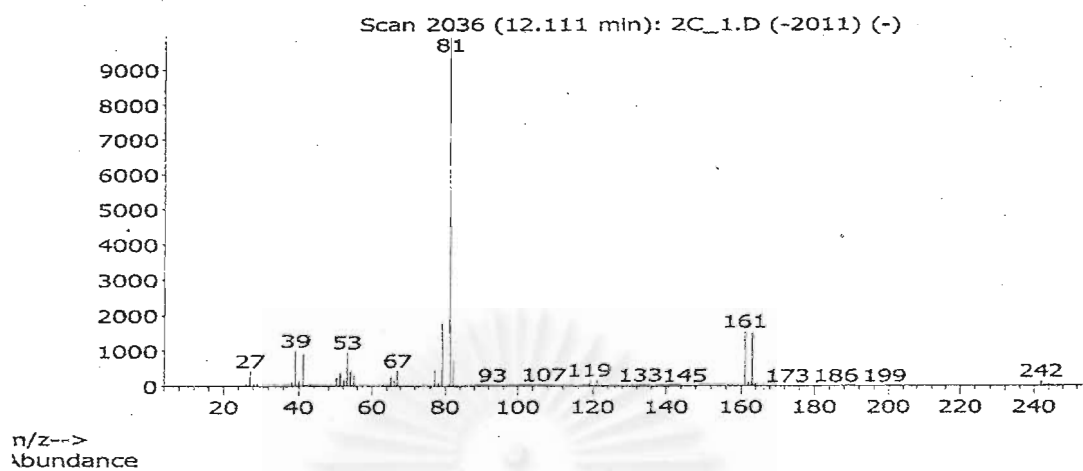


Figure B13 The mass spectrum of mixture 2C at  $t_R = 12.11$  min

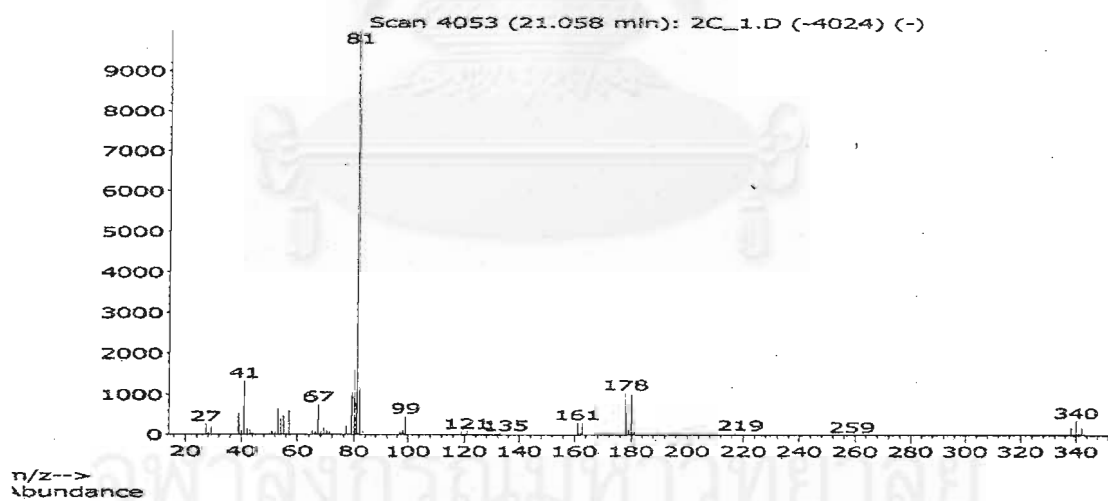


Figure B14 The mass spectrum of mixture 2C at  $t_R = 21.01$  min

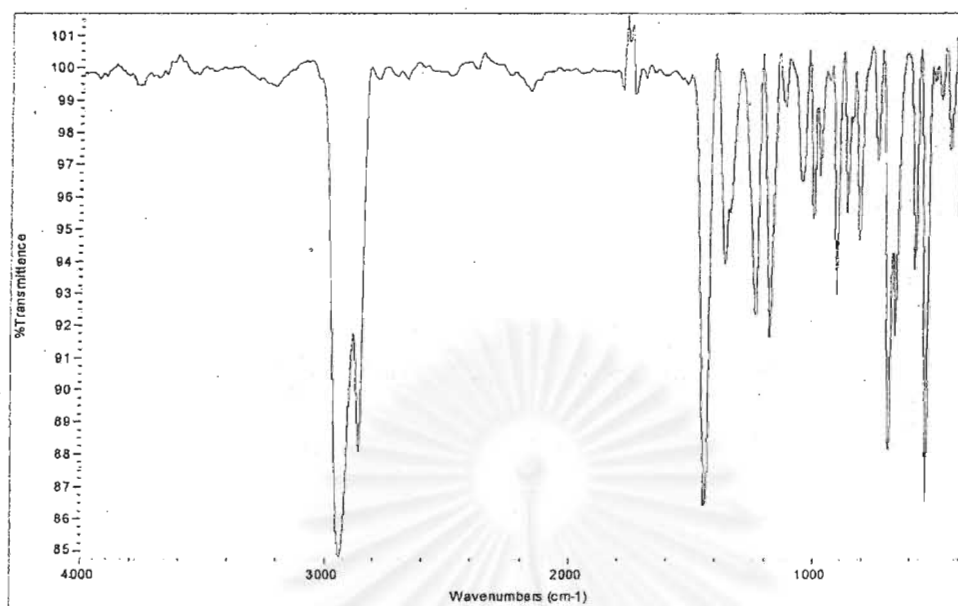


Figure B15 The FTIR spectrum of mixture 3C

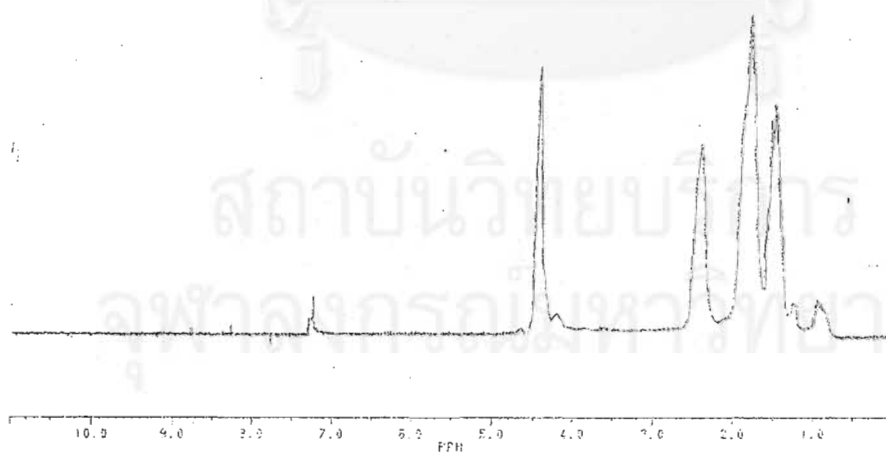


Figure B16 The <sup>1</sup>H-NMR spectrum of mixture 3C

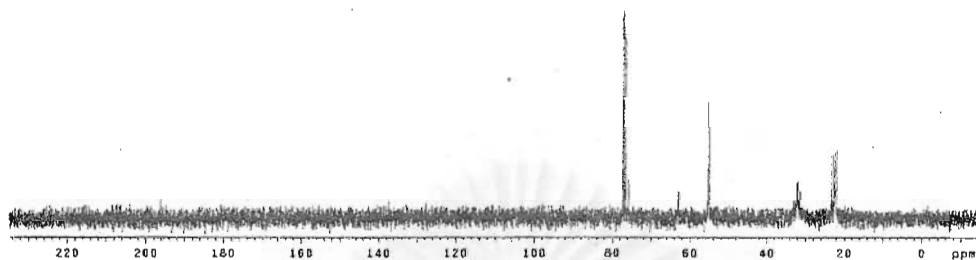


Figure B17 The  $^{13}\text{C}$ -NMR spectrum of mixture 3C

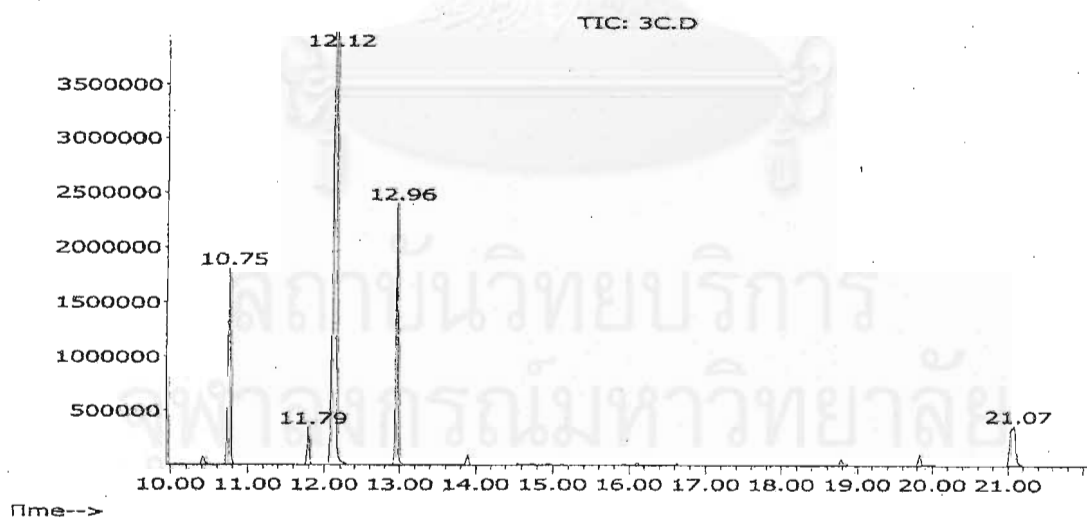


Figure B18 The gas chromatogram of mixture 3C



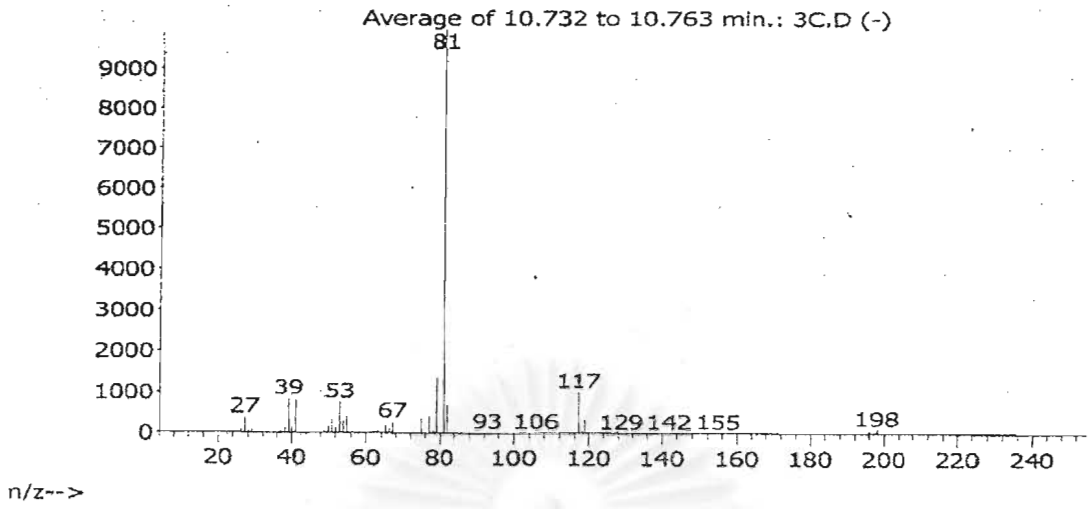


Figure B19 The mass spectrum of mixture 3C at  $t_R = 10.73$  min

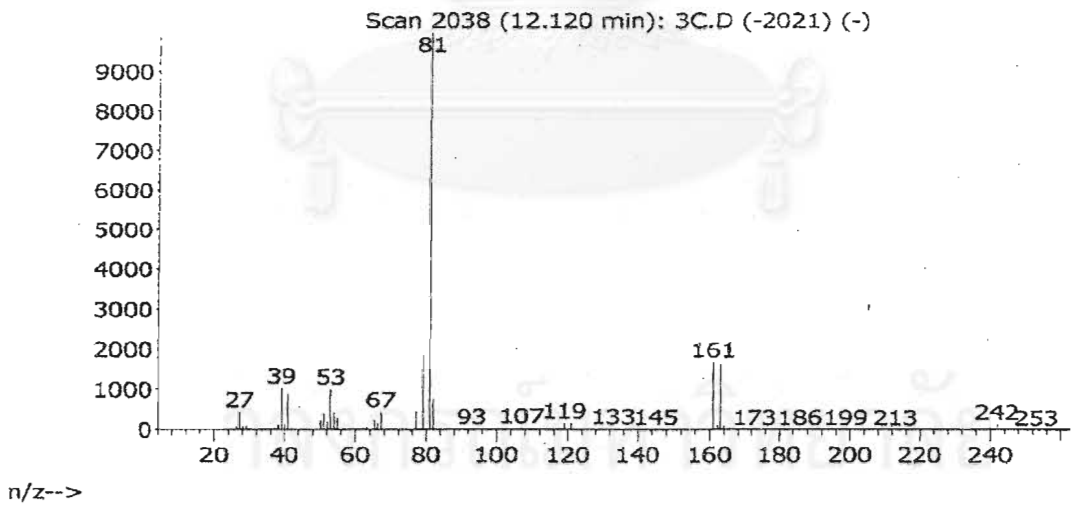


Figure B20 The mass spectrum of mixture 3C at  $t_R = 12.12$  min

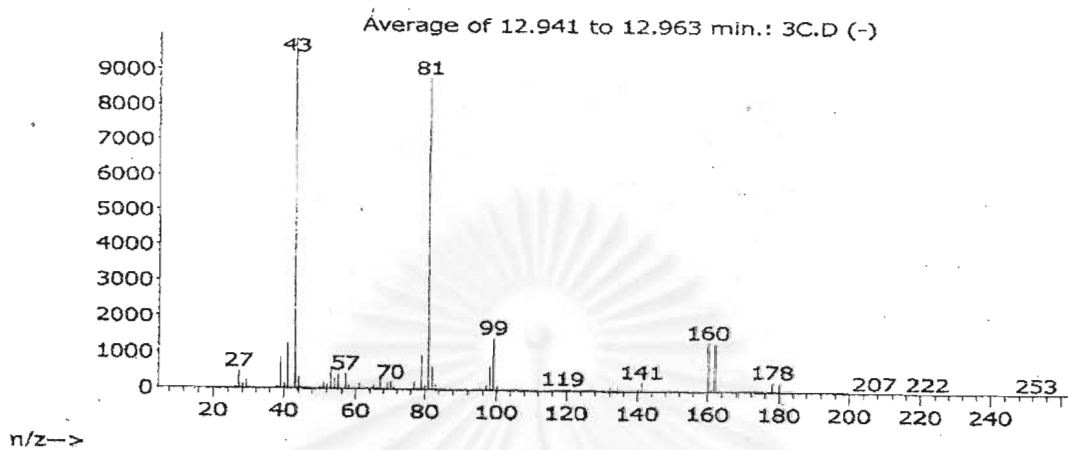


Figure B21 The mass spectrum of mixture 3C at  $t_R = 12.96$  min

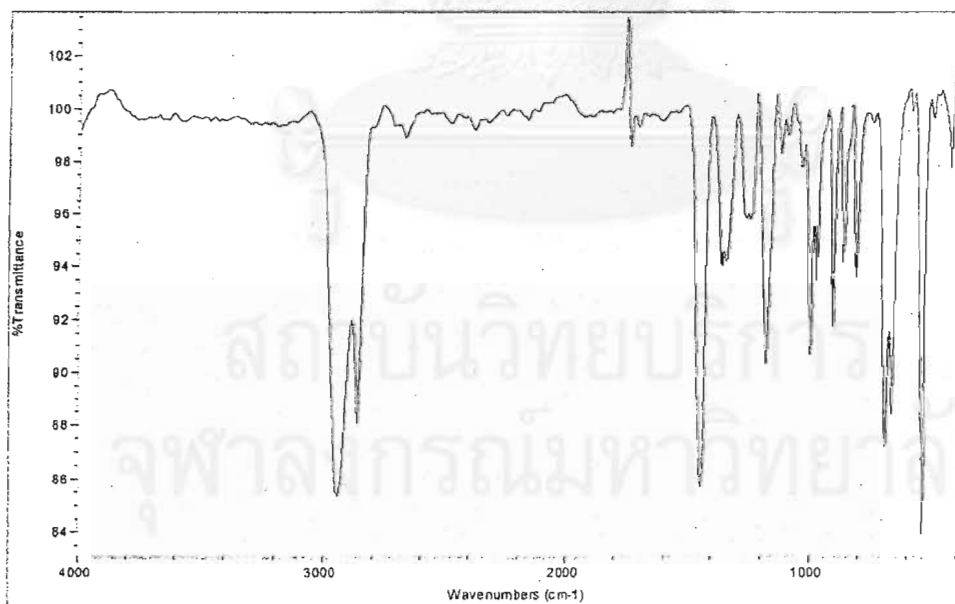


Figure B22 The FTIR spectrum of mixture 4C

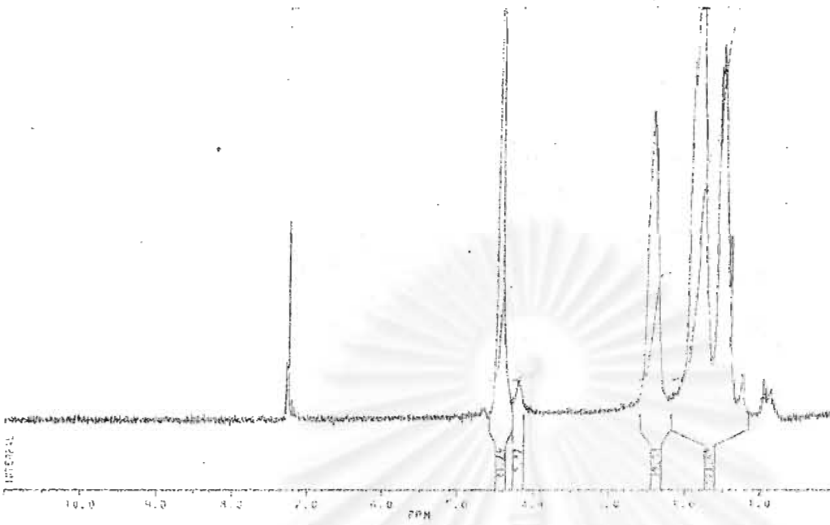


Figure B23 The  $^1\text{H-NMR}$  spectrum of mixture 4C

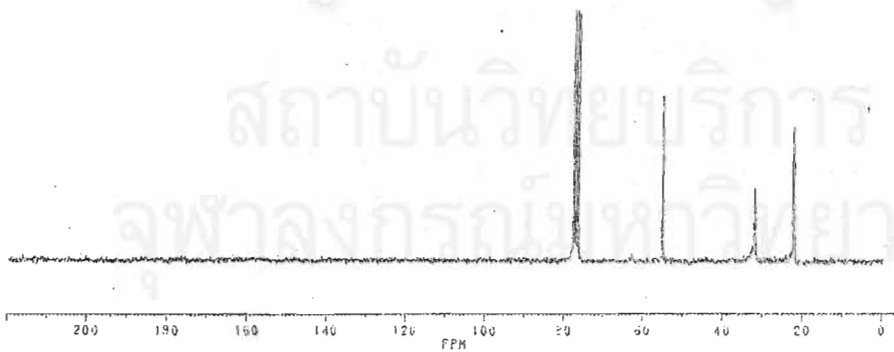
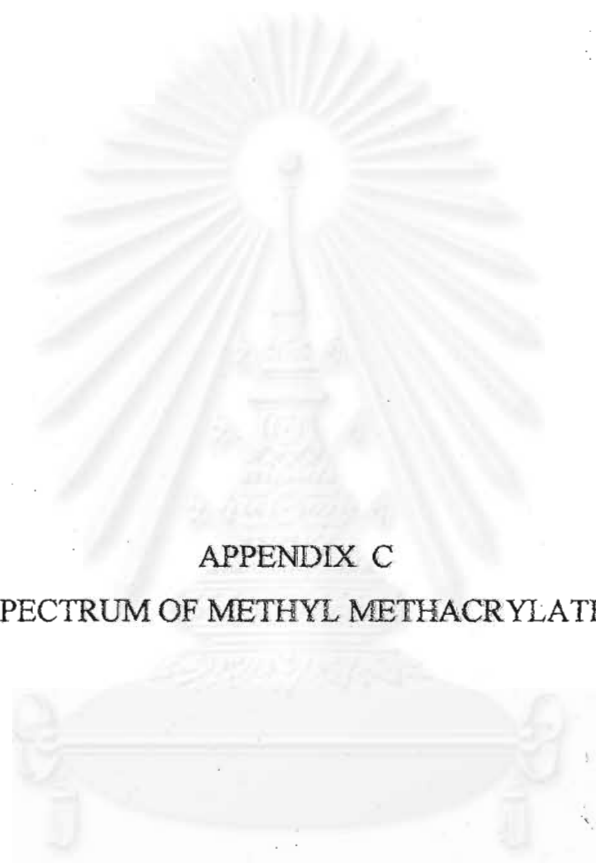


Figure B24 The  $^{13}\text{C-NMR}$  spectrum of mixture 4C



APPENDIX C  
SPECTRUM OF METHYL METHACRYLATE

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

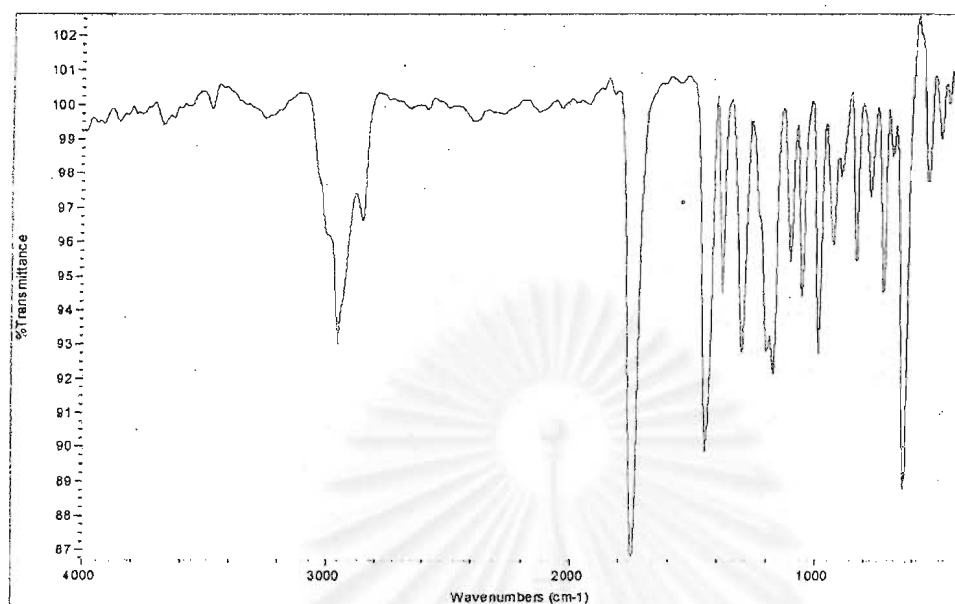


Figure C1 The FTIR spectrum of mixture 1M

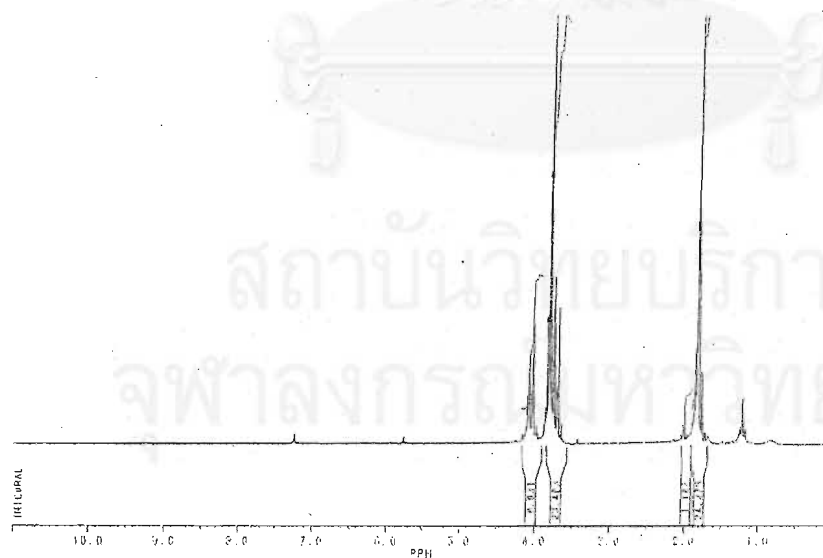


Figure C2 The <sup>1</sup>H-NMR spectrum of mixture 1M

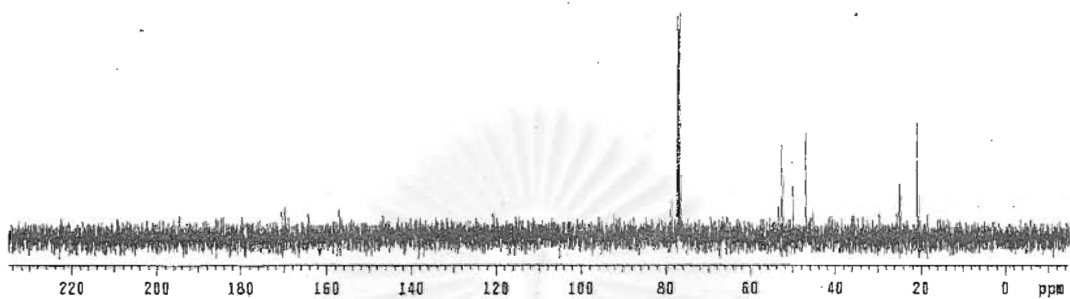


Figure C3 The  $^{13}\text{C}$ -NMR spectrum of mixture 1M

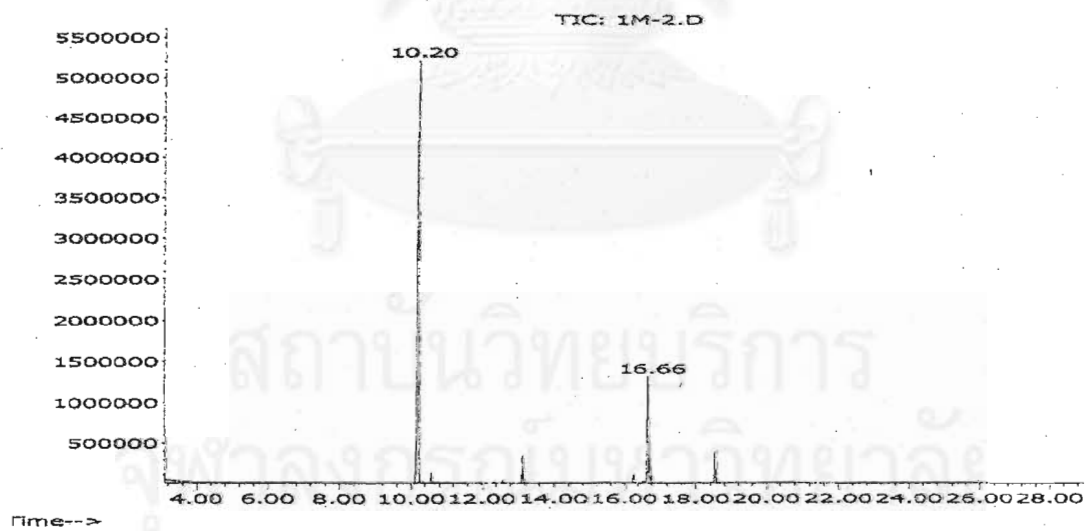


Figure C4 The gas chromatogram of mixture 1M

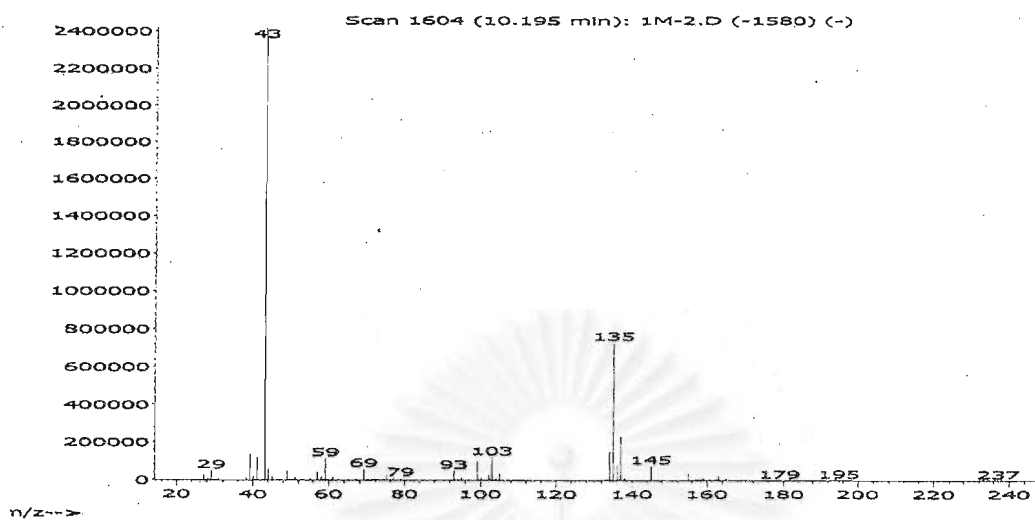


Figure C5 The mass spectrum of mixture 1M at  $t_R = 10.19$  min

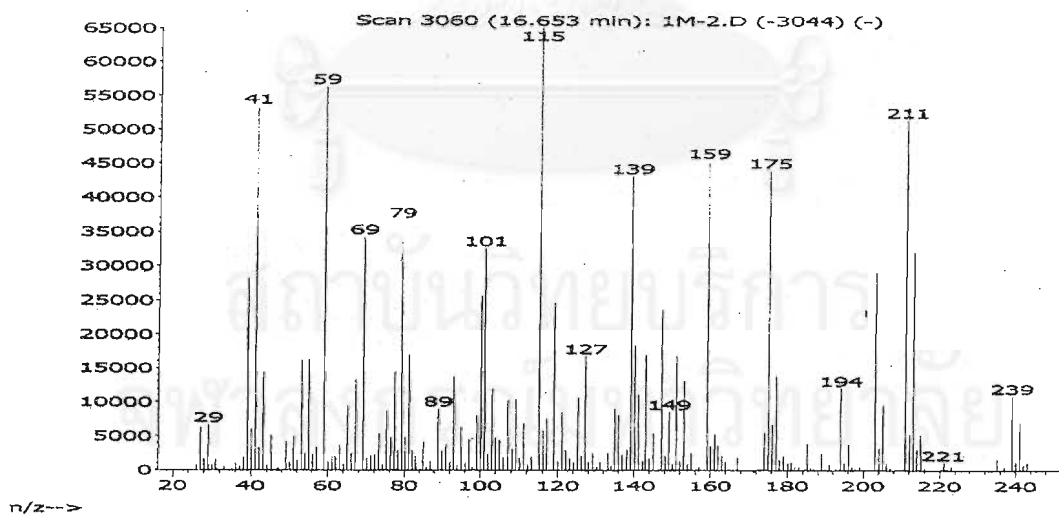


Figure C6 The mass spectrum of mixture 1M at  $t_R = 16.65$  min

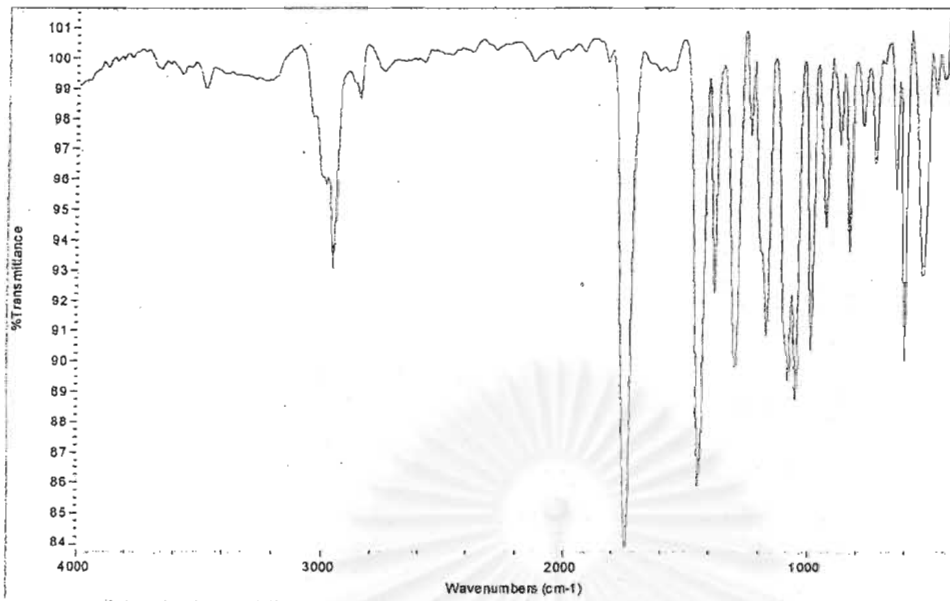


Figure C7 The FTIR spectrum of mixture 2M

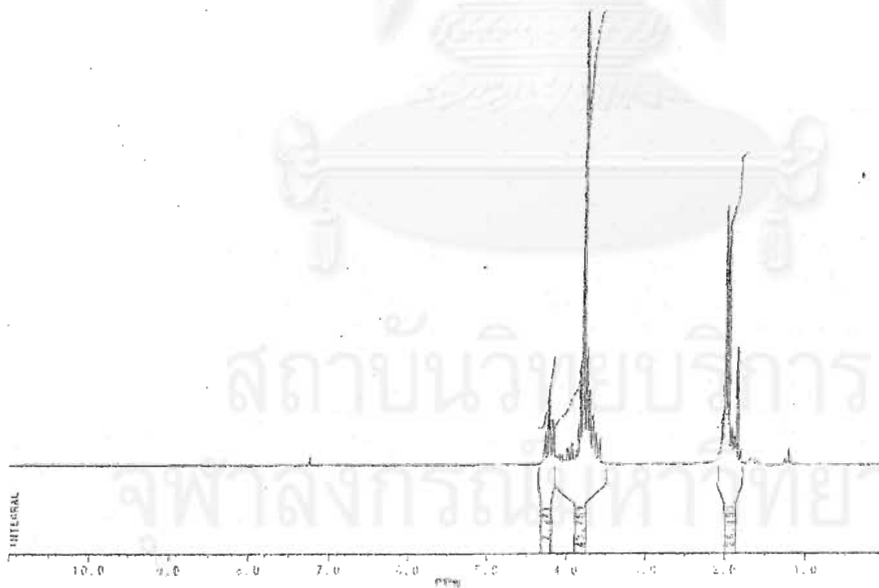


Figure C8 The <sup>1</sup>H-NMR spectrum of mixture 2M



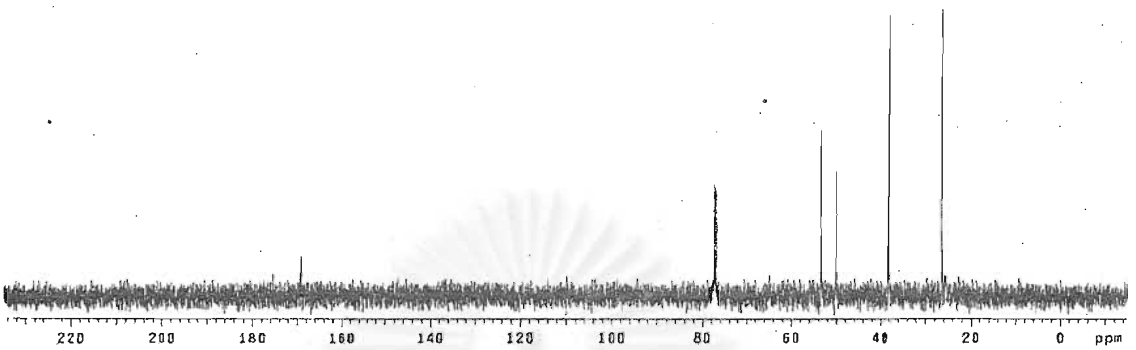


Figure C9 The  $^{13}\text{C}$ -NMR spectrum of mixture 2M

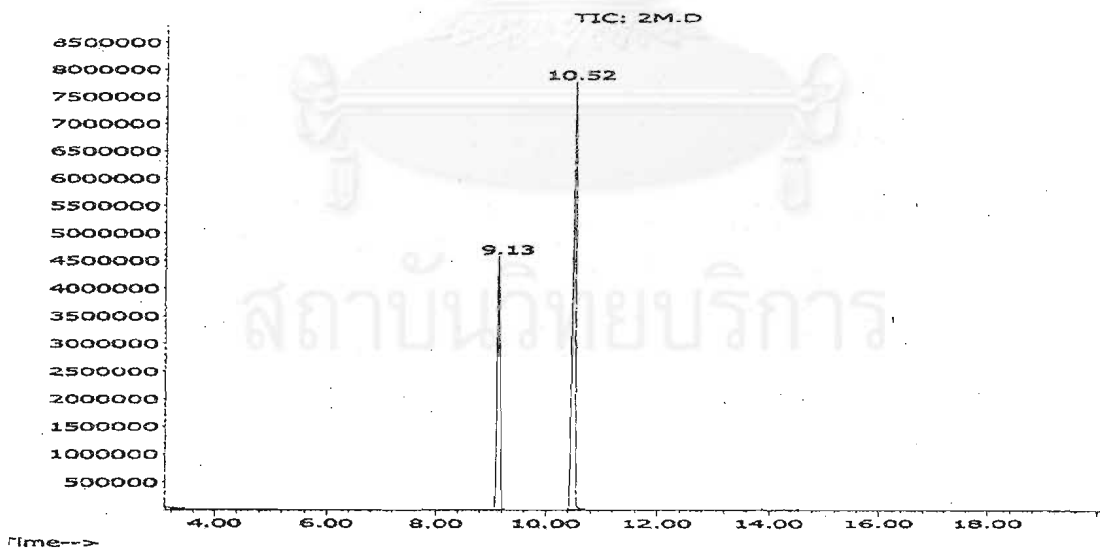


Figure C10 The gas chromatogram of mixture 2M

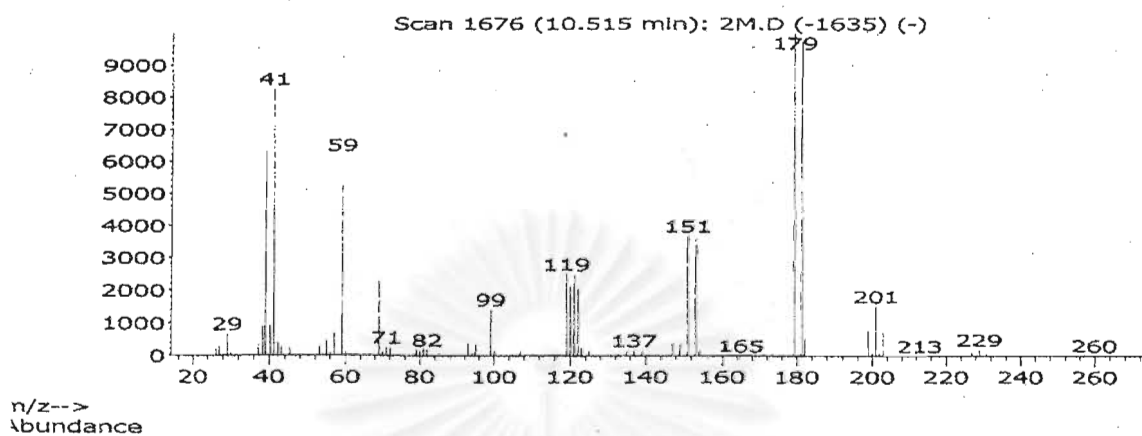


Figure C11 The mass spectrum of mixture 2M at  $t_R = 10.51$  min

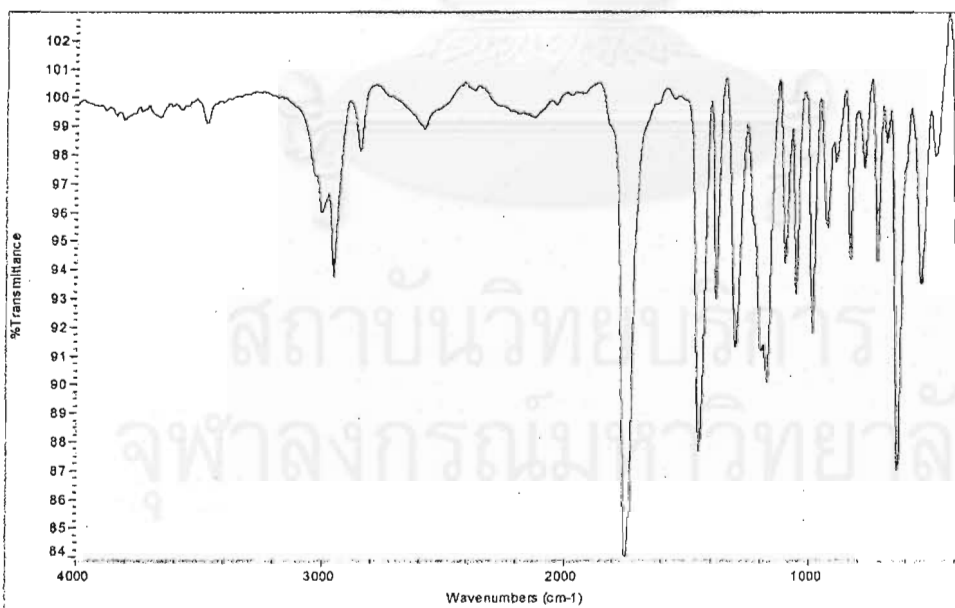


Figure C12 The FTIR spectrum of mixture 3M

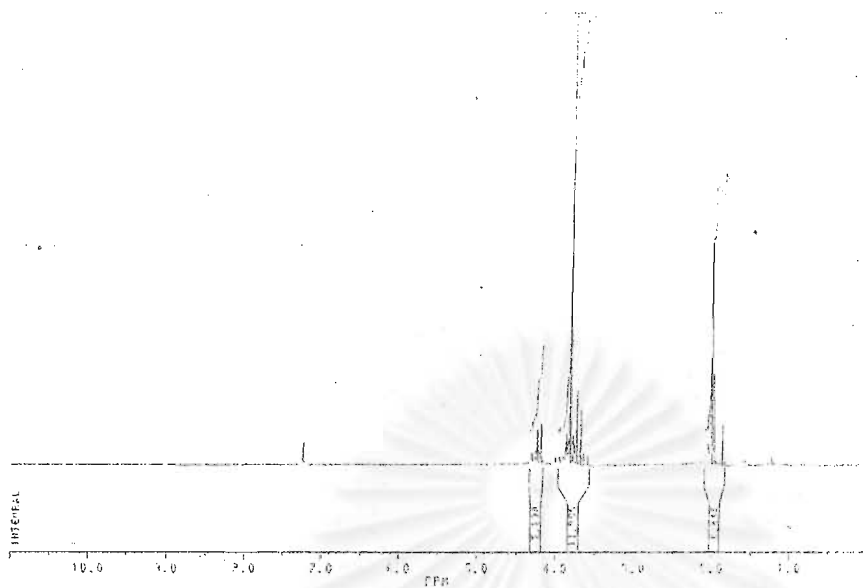


Figure C13 The  $^1\text{H-NMR}$  spectrum of mixture 3M

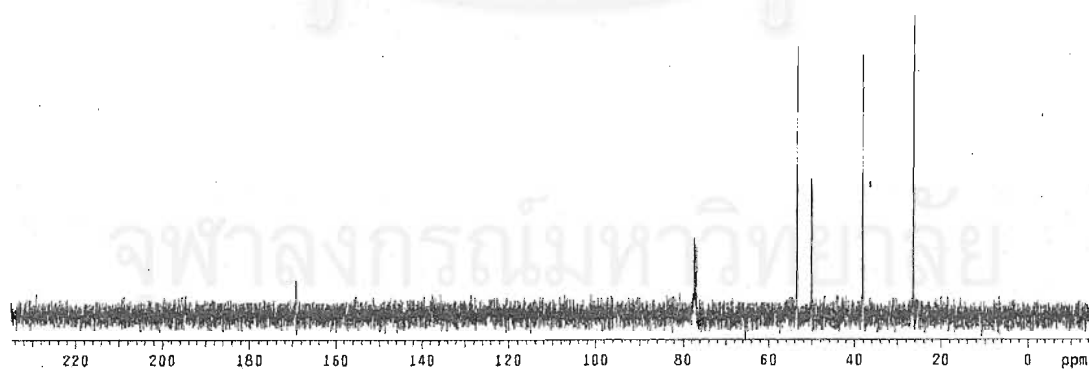


Figure C14 The  $^{13}\text{C-NMR}$  spectrum of mixture 3M

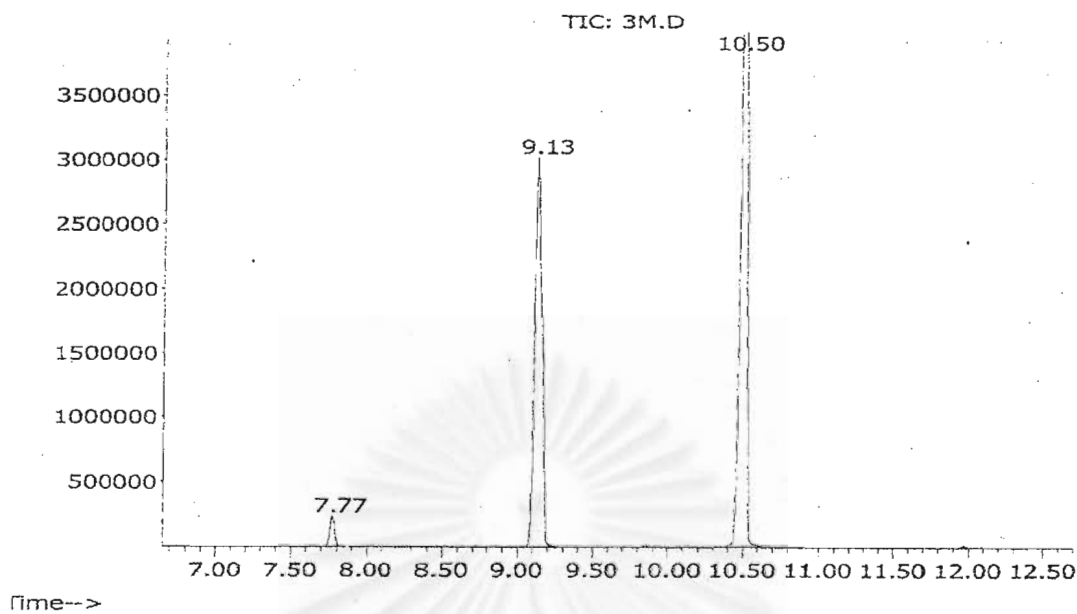


Figure C15 The gas chromatogram of mixture 3M

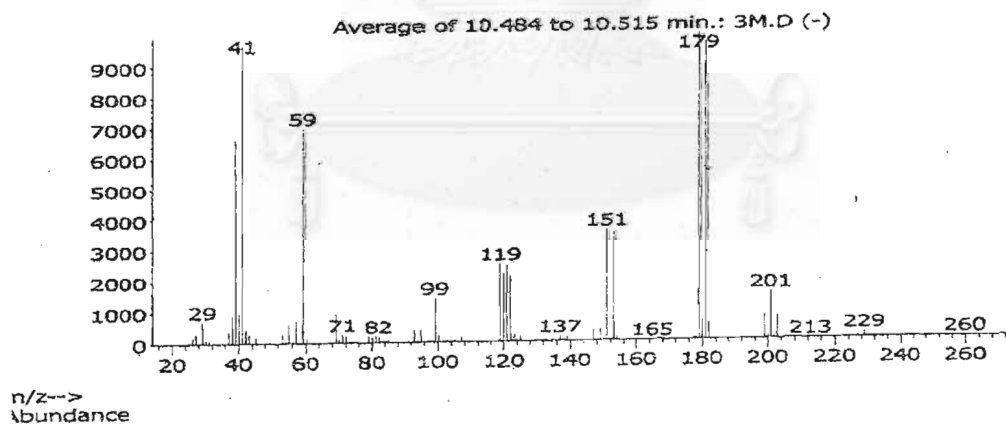


Figure C16 The mass spectrum of mixture 3M at  $t_R = 10.48$  min

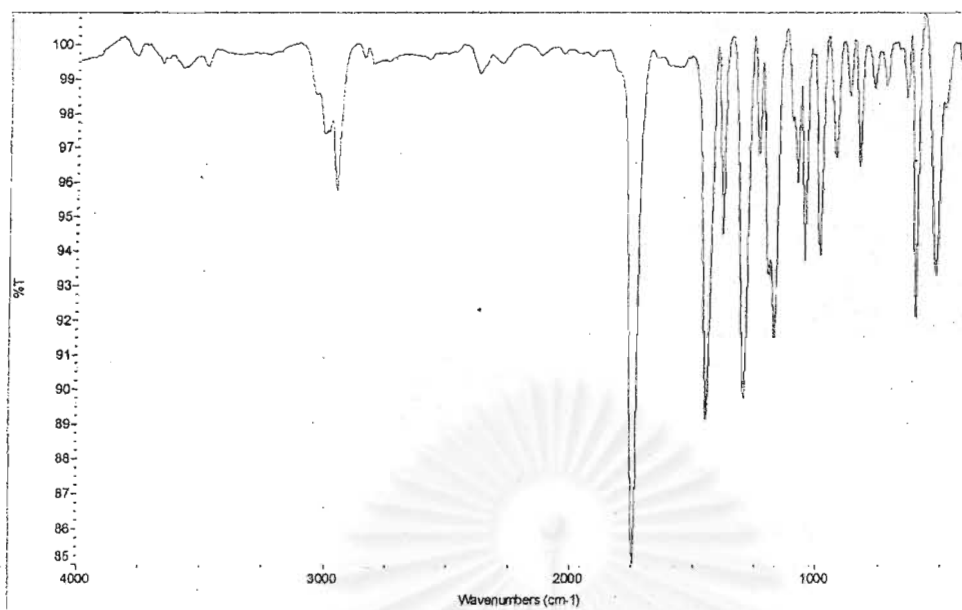


Figure C17 The FTIR spectrum of mixture 4M

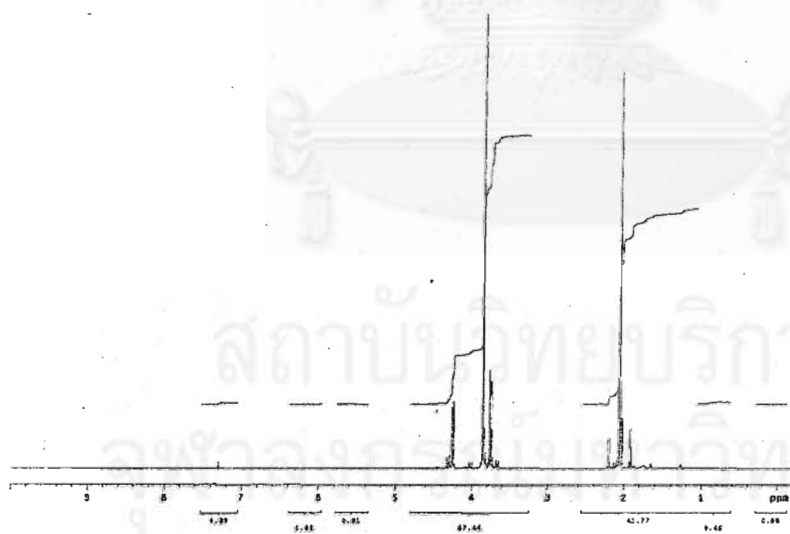


Figure C18 The <sup>1</sup>H-NMR spectrum of mixture 4M

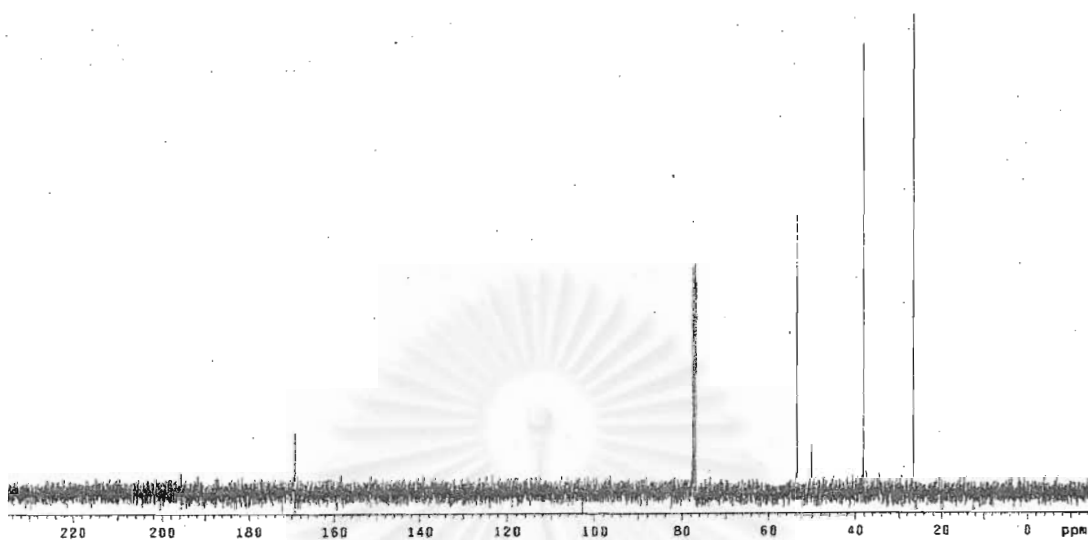


Figure C19 The  $^{13}\text{C}$ -NMR spectrum of mixture 4M

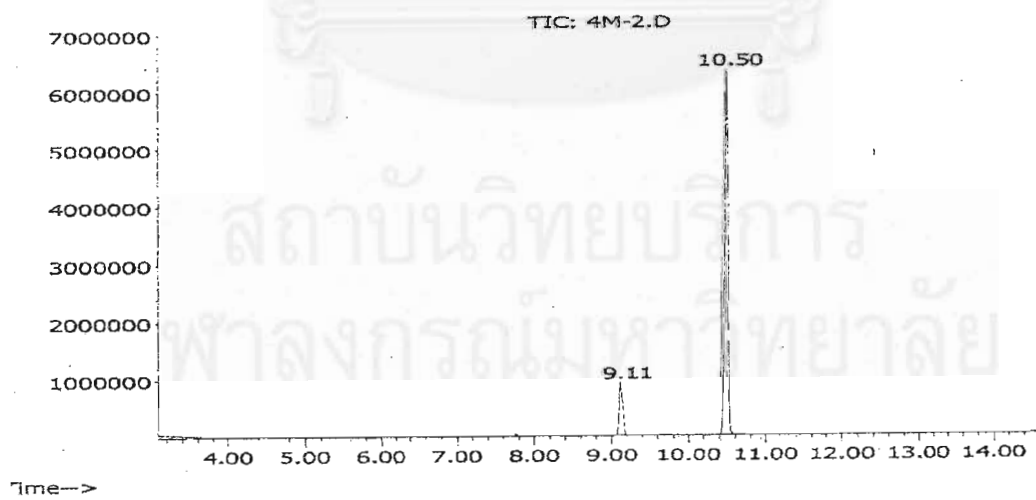


Figure C20 The gas chromatogram of mixture 4M

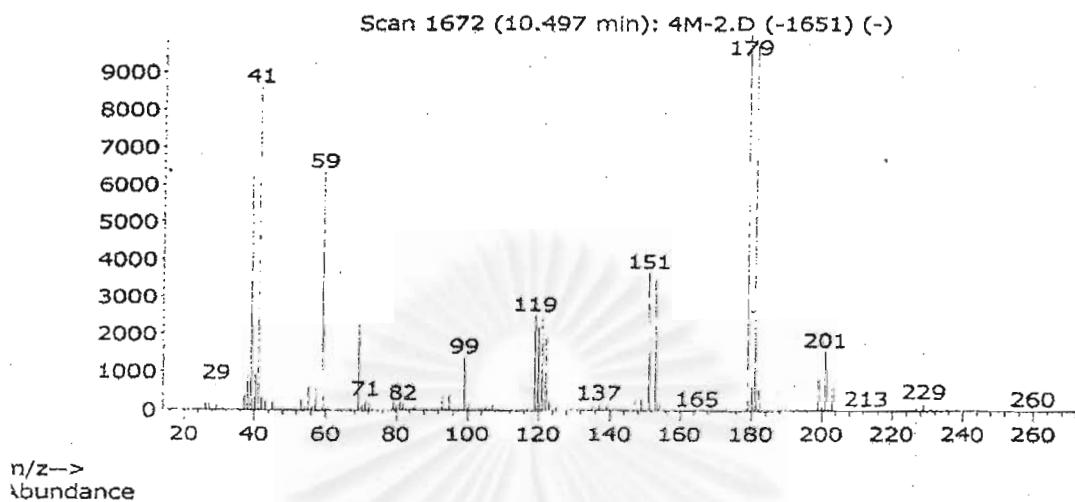
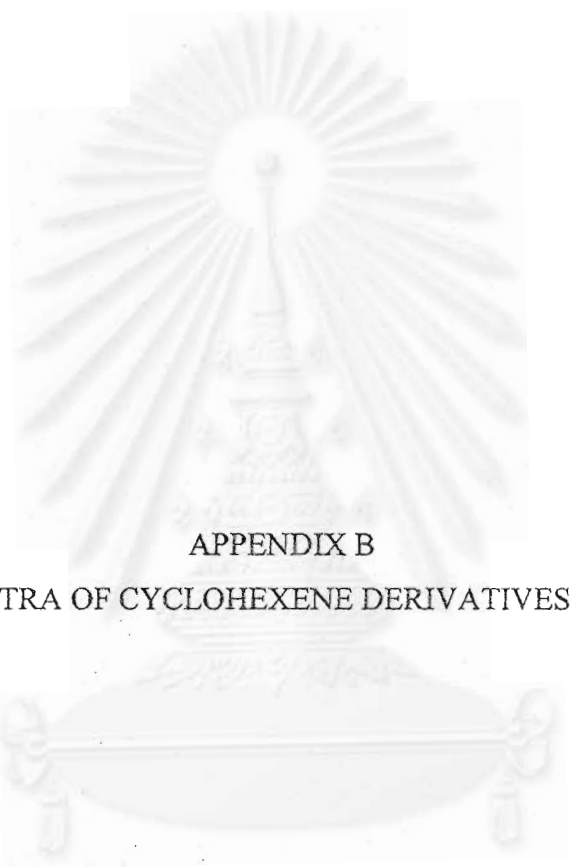


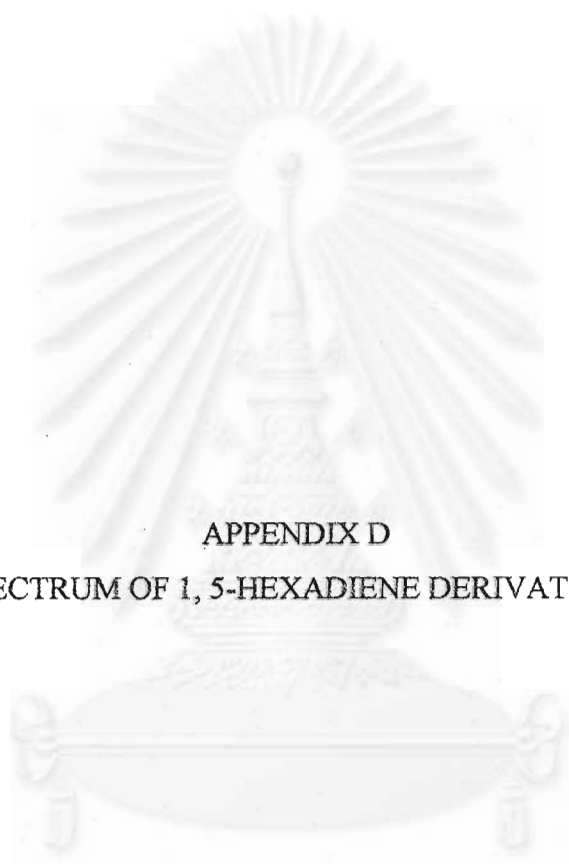
Figure C21 The mass spectrum of mixture 4M at  $t_R = 10.49$  min



APPENDIX B  
SPECTRA OF CYCLOHEXENE DERIVATIVES

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย





APPENDIX D  
SPECTRUM OF 1, 5-HEXADIENE DERIVATIVES

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

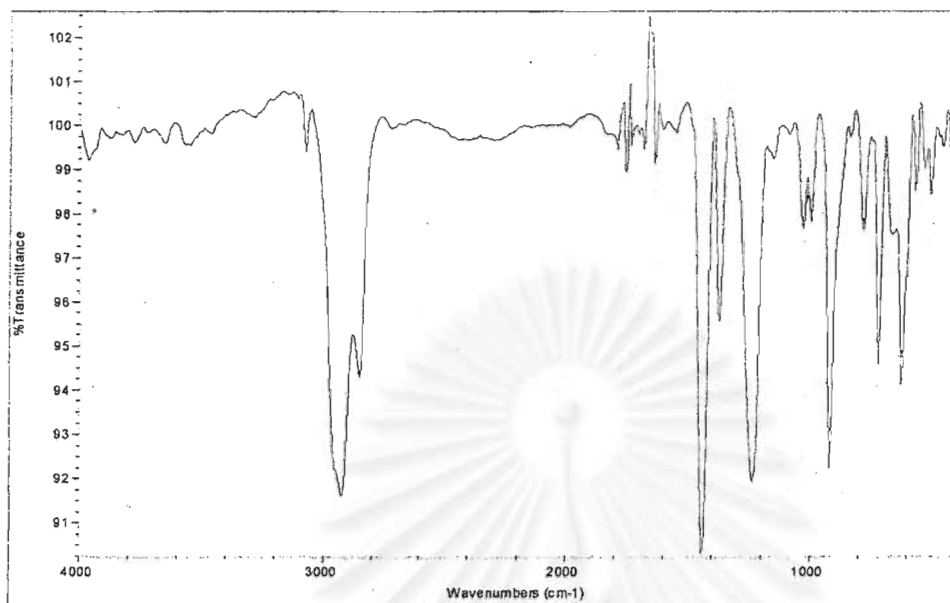


Figure D1 The FTIR spectrum of mixture 1HD

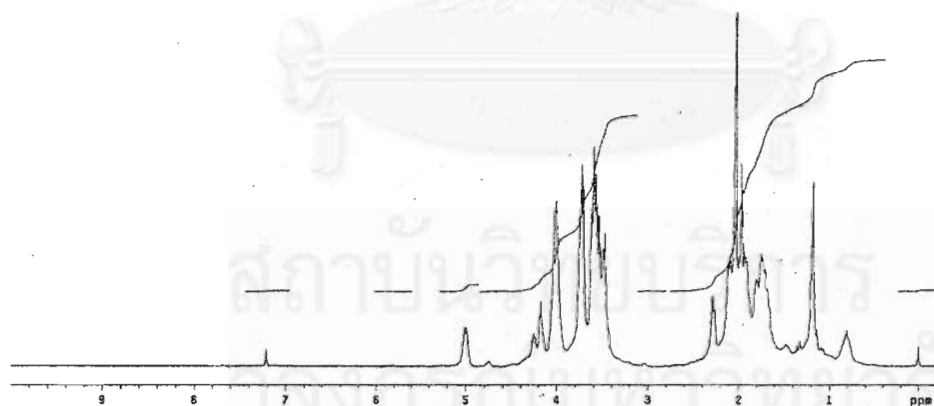


Figure D2 The <sup>1</sup>H-NMR spectrum of mixture 1HD

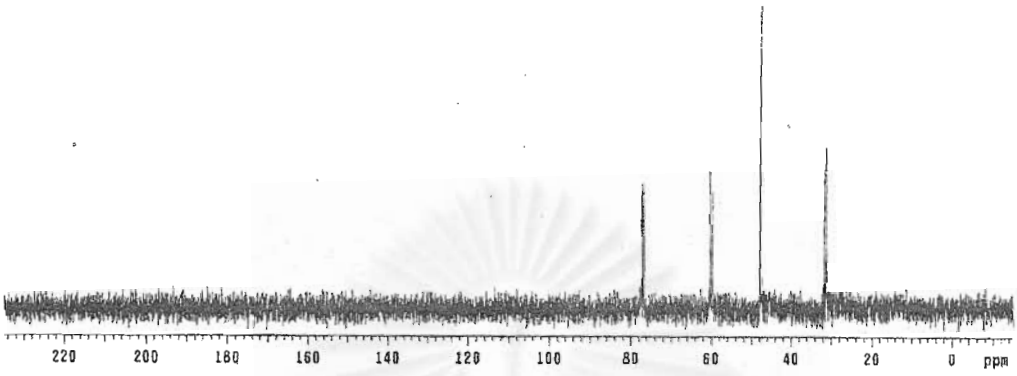


Figure D3 The <sup>13</sup>C-NMR spectrum of mixture 1HD

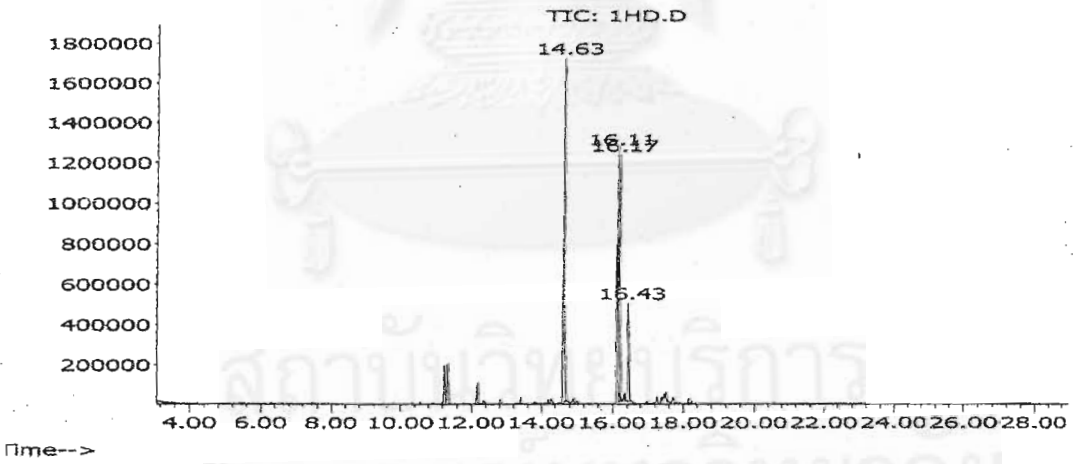


Figure D4 The gas chromatogram of mixture 1HD

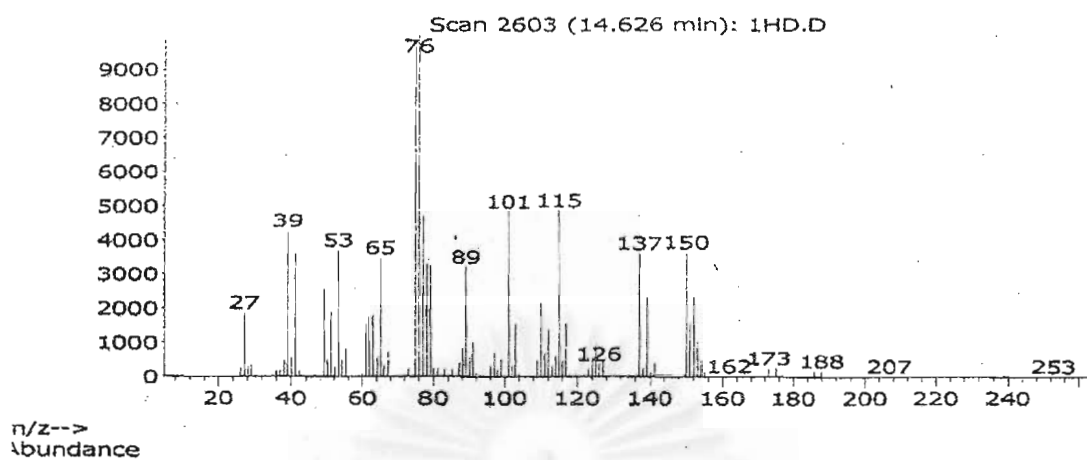


Figure D5 The mass spectrum of mixture 1HD at  $t_R = 14.62$  min

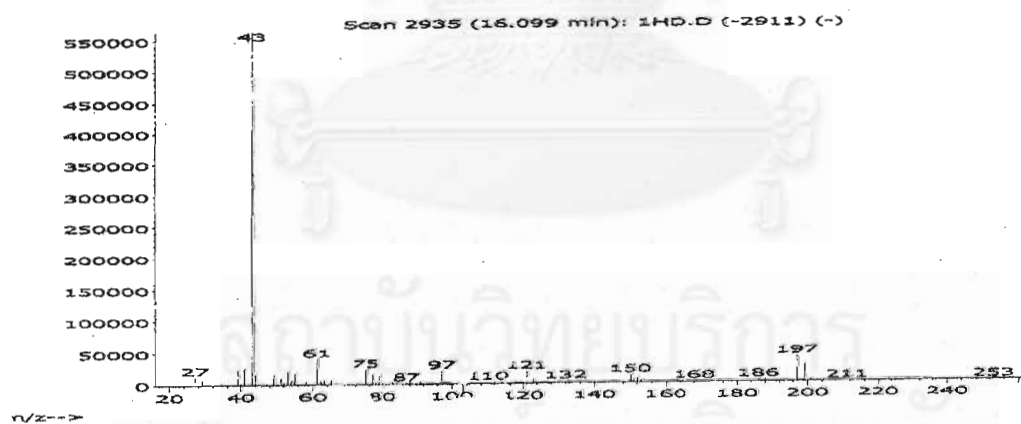


Figure D6 The mass spectrum of mixture 1HD at  $t_R = 16.10$  min

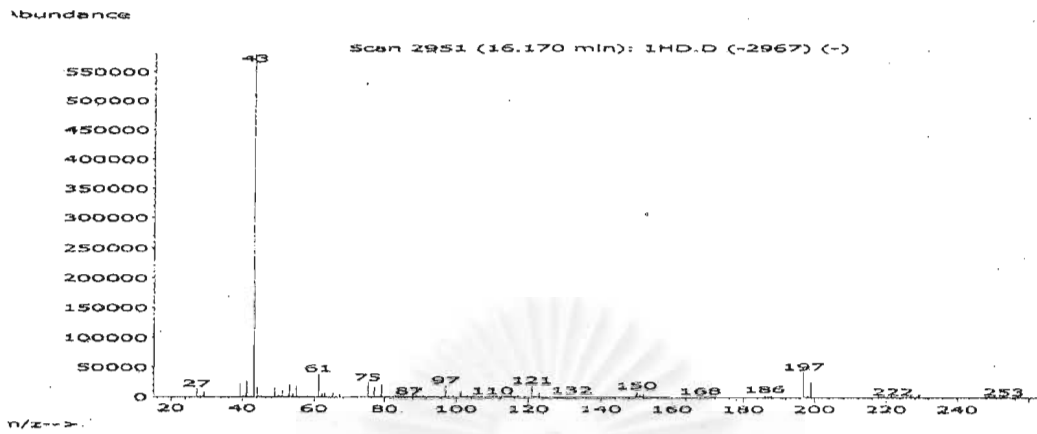


Figure D7 The mass spectrum of mixture 1HD at  $t_R = 16.17$  min

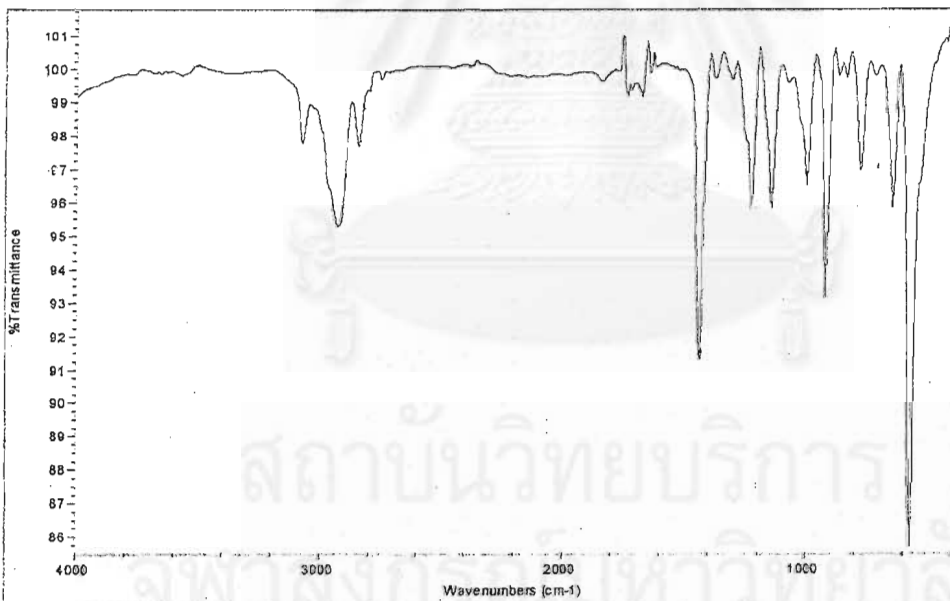


Figure D8 The FTIR spectrum of mixture 2HD

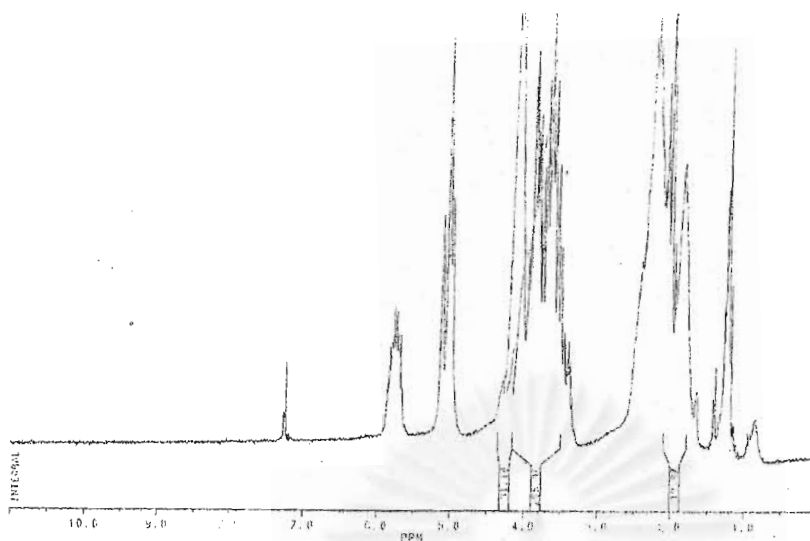


Figure D9 The  $^1\text{H}$ -NMR spectrum of mixture 2HD

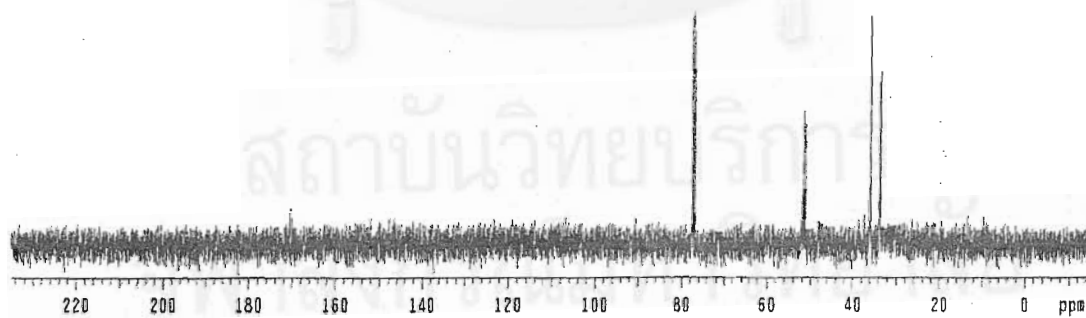


Figure D10 The  $^{13}\text{C}$ -NMR spectrum of mixture 2HD

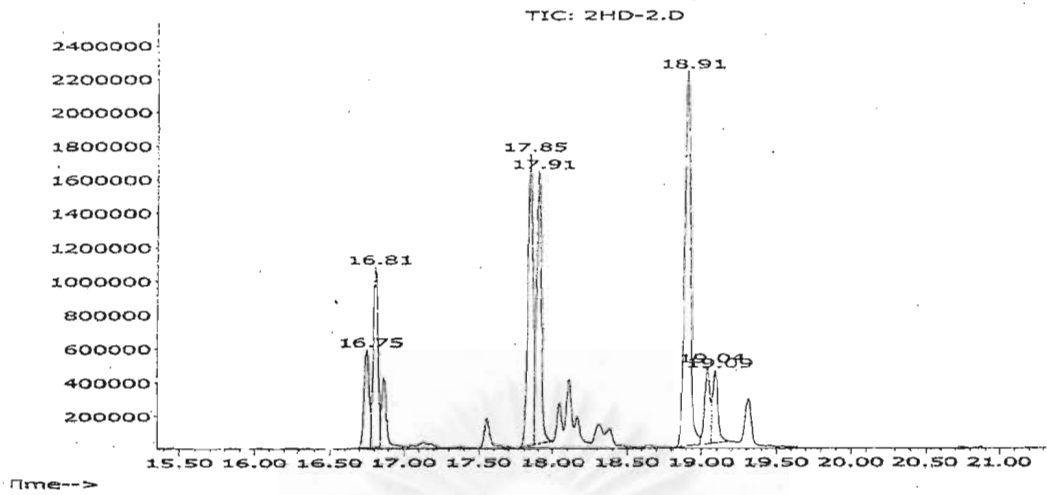


Figure D11 The gas chromatogram of mixture 2HD

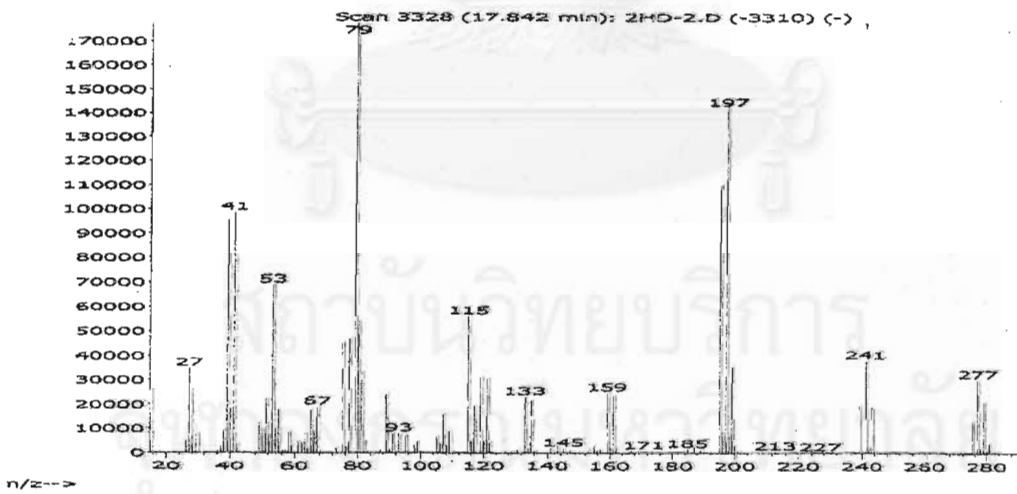


Figure D12 The mass spectrum of mixture 2HD at  $t_R = 17.84$  min

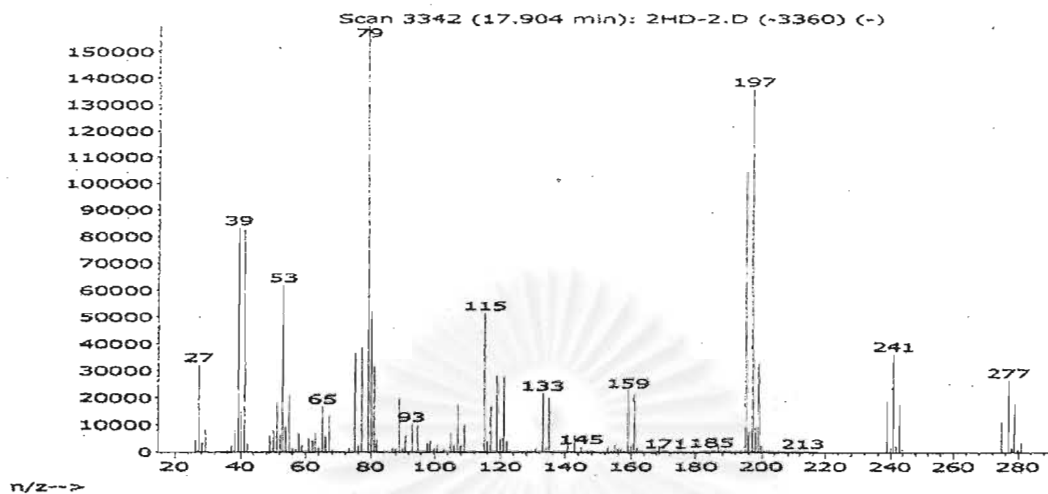


Figure D13 The mass spectrum of mixture 2HD at  $t_R = 17.90$  min

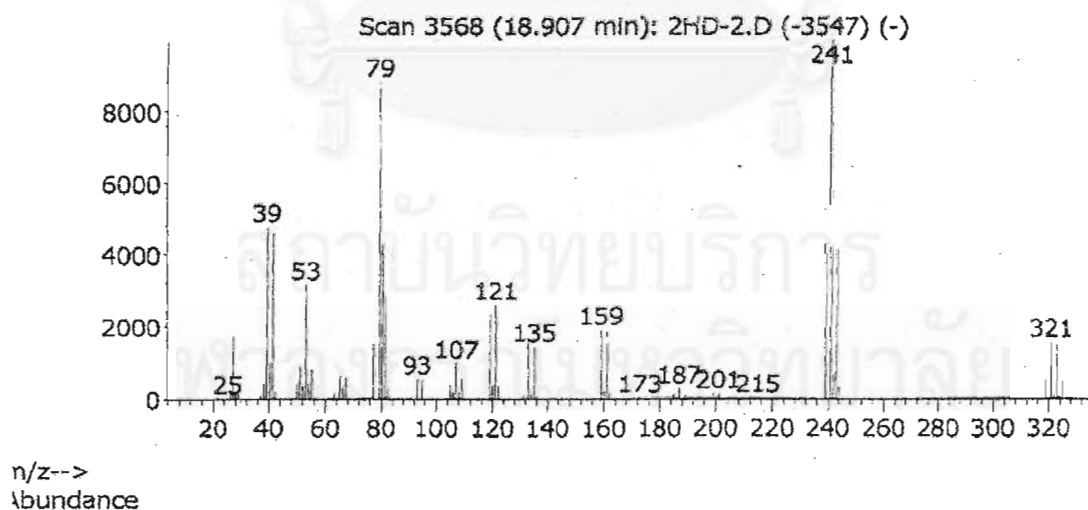


Figure D14 The mass spectrum of mixture 2HD at  $t_R = 18.91$  min



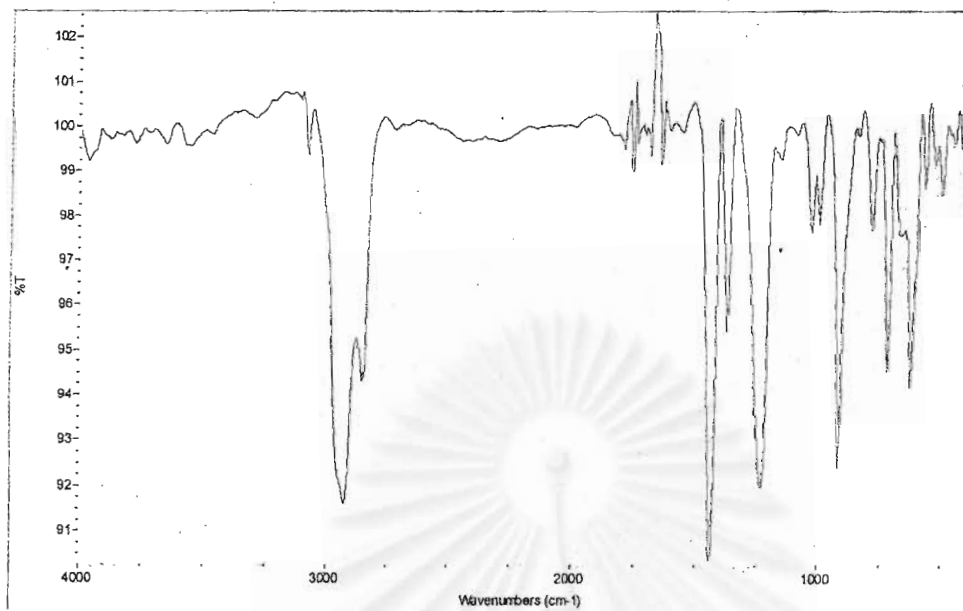


Figure D15 The FTIR spectrum of mixture 3HD

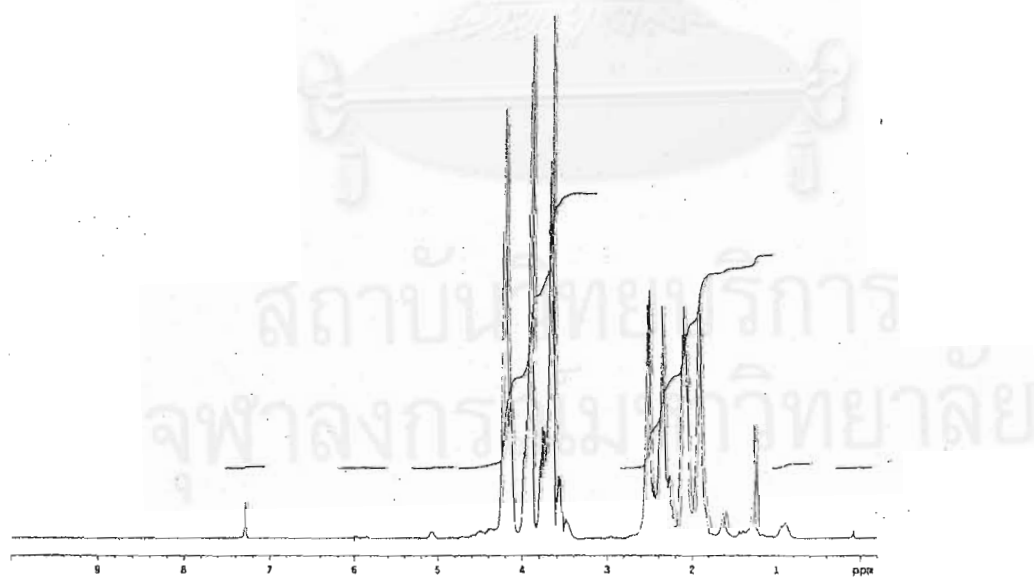


Figure D16 The <sup>1</sup>H-NMR spectrum of mixture 3HD

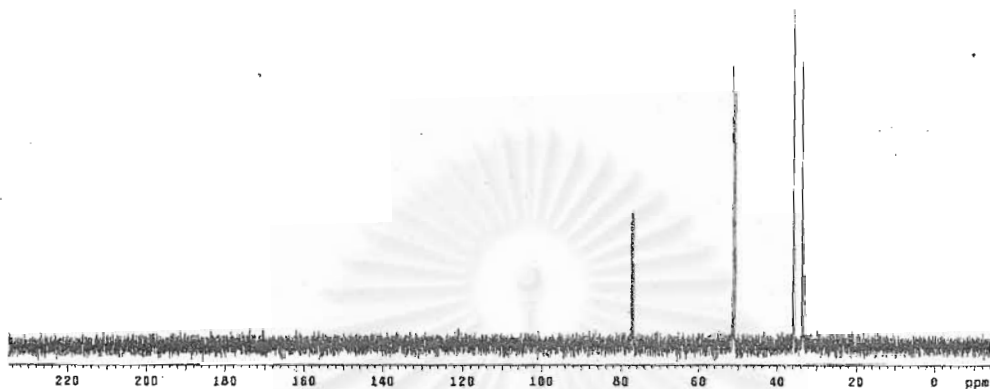


Figure D17 The  $^{13}\text{C}$ -NMR spectrum of mixture 3HD

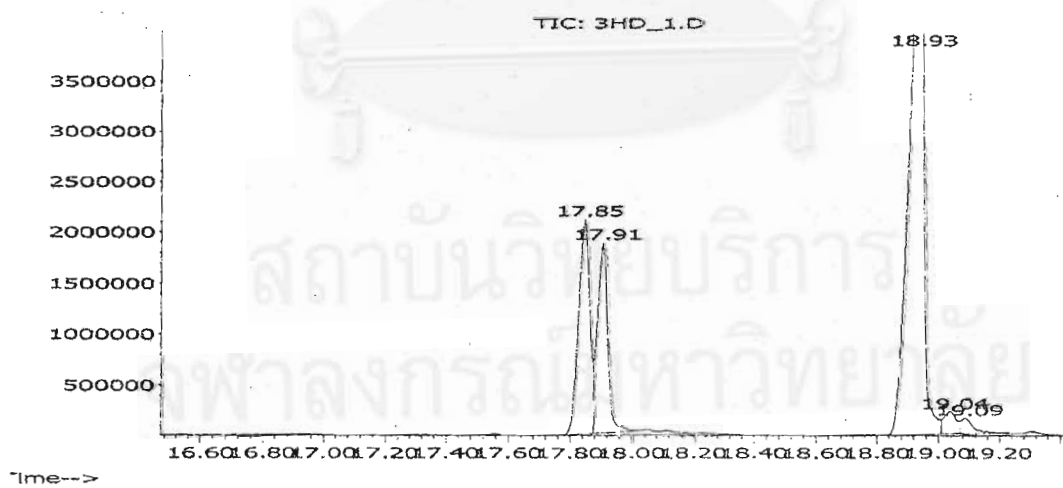


Figure D18 The gas chromatogram of mixture 3HD

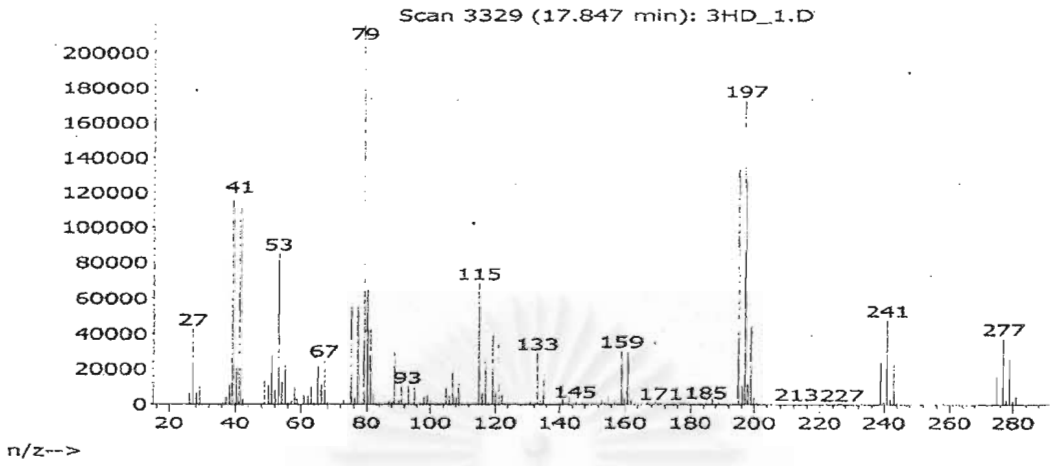


Figure D19 The mass spectrum of mixture 3HD at  $t_R = 17.84$  min

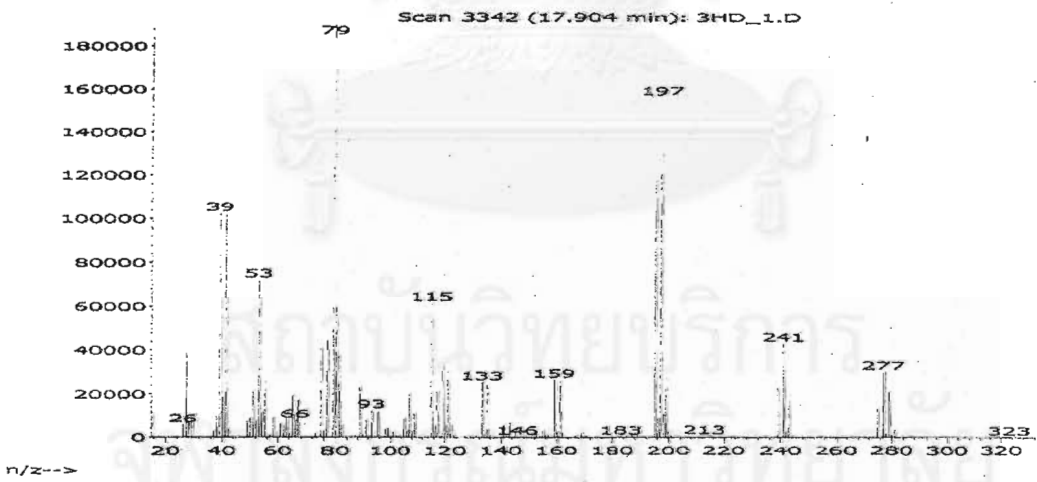


Figure D17 The mass spectrum of mixture 3HD at  $t_R = 17.90$  min

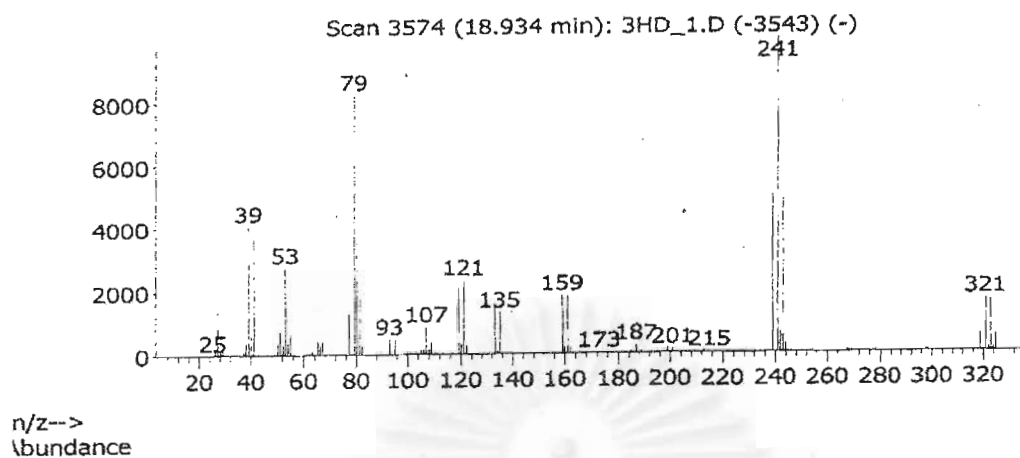


Figure D18 The mass spectrum of mixture 3HD at  $t_R = 18.93$  min

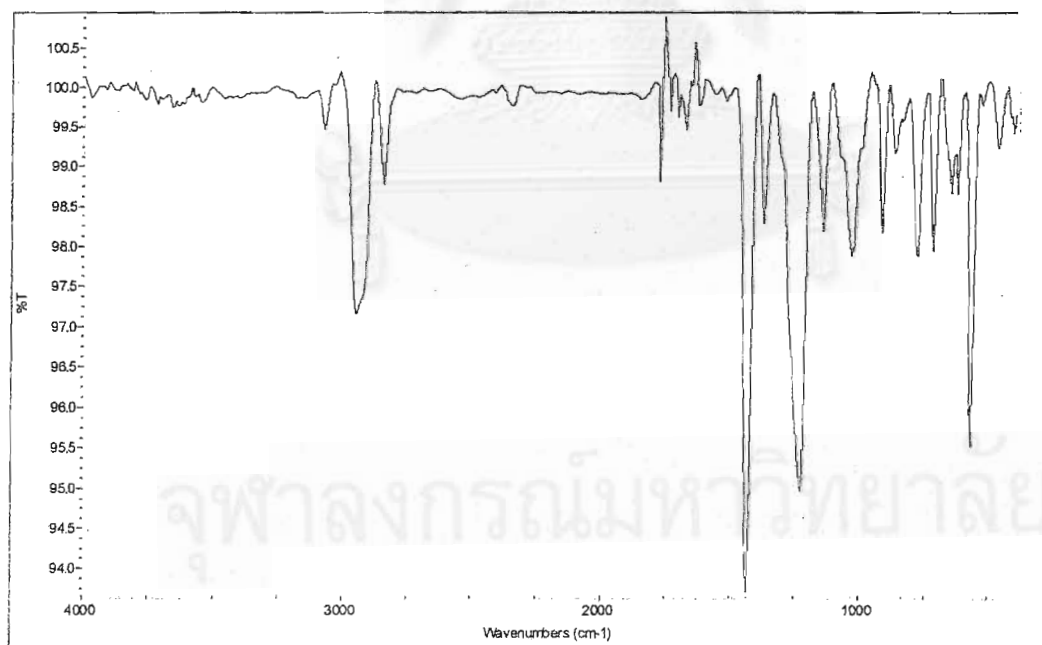


Figure D19 The FTIR spectrum of mixture 4HD

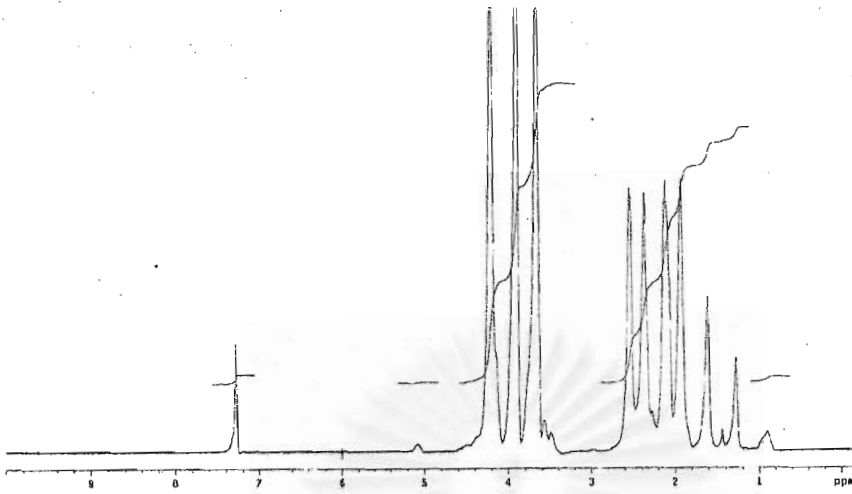


Figure D20 The  $^1\text{H}$ -NMR spectrum of mixture 4HD

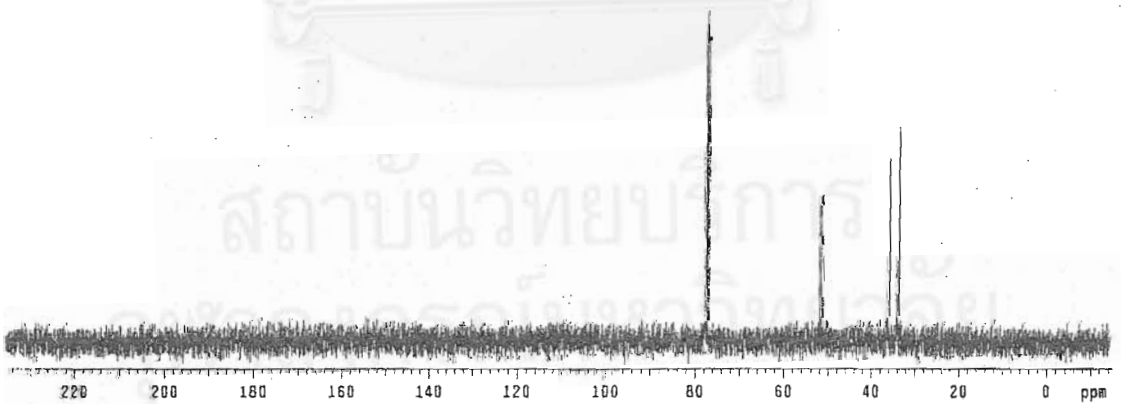


Figure D21 The  $^{13}\text{C}$ -NMR spectrum of mixture 4HD

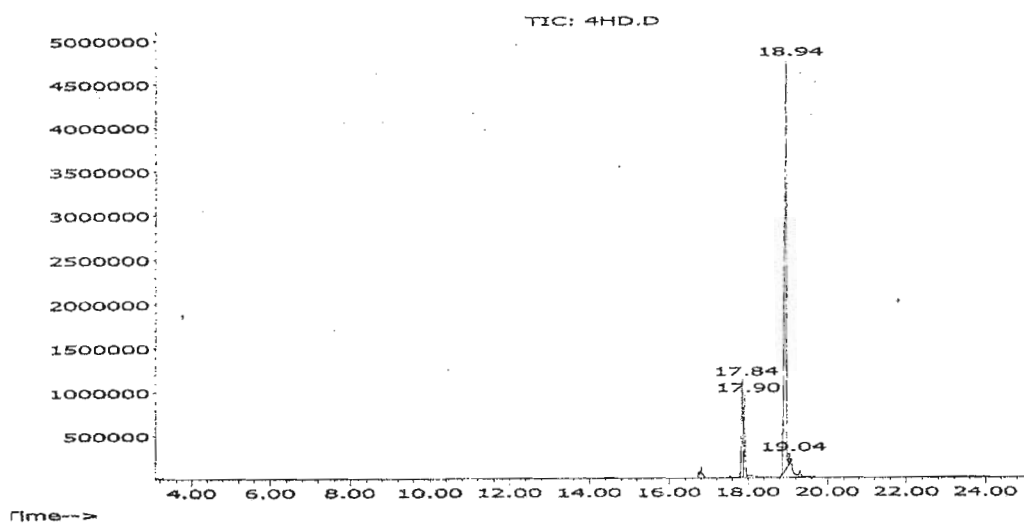


Figure D22 The gas chromatogram of mixture 4HD

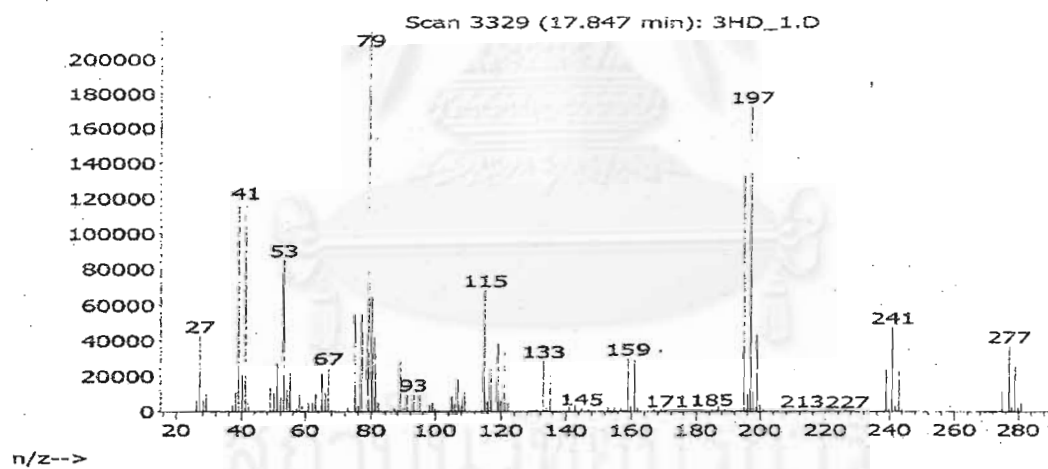


Figure D23 The mass spectrum of mixture 4HD at  $t_R = 17.84$  min

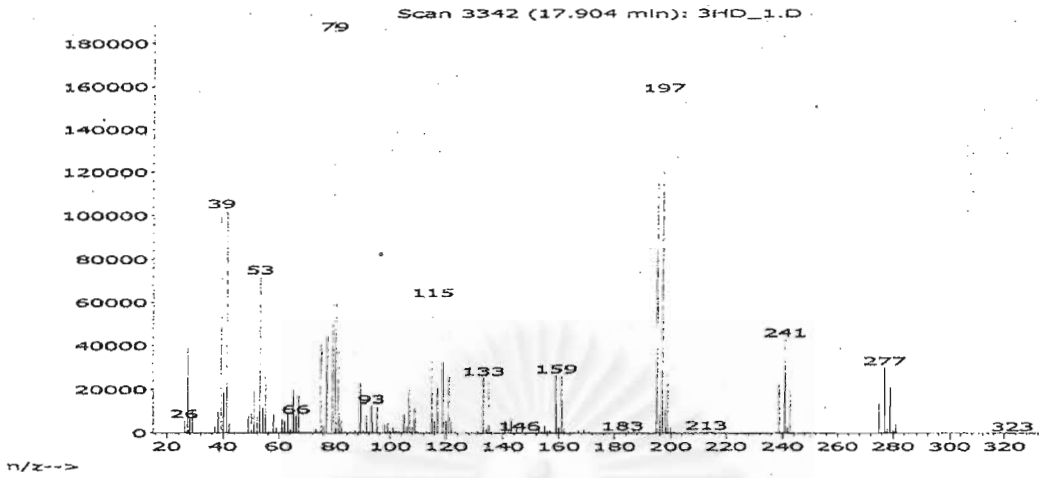


Figure D24 The mass spectrum of mixture 4HD at  $t_R = 17.90$  min

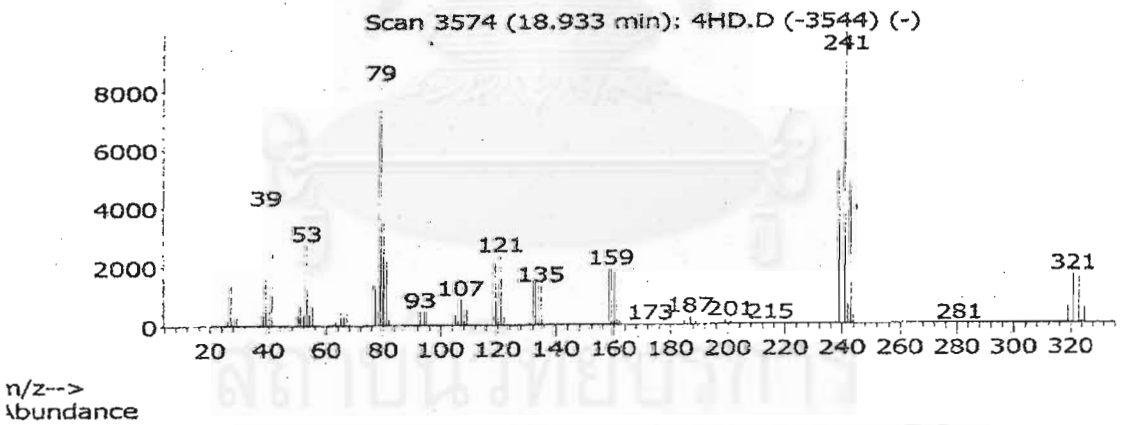


Figure D25 The mass spectrum of mixture 4HD at  $t_R = 18.93$  min

## VITA

Ms. Navaluck Dulayasuwan was born on March 15, 1980 in Rachaburi, Thailand. She received her Bachelor's Degree of Science in Chemistry from Silpakorn University in 2000. She continued her Master's Degree of Science in Petrochemistry and Polymer Science, Faculty of Science at Chulalongkorn University in 2001 and finished the M. Sc. degree in 2005.



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย